RAPID COMMUNICATION

Significant photoelectrical response of epitaxial graphene grown on Si-terminated 6H-SiC*

Hao Xin(郝 昕), Chen Yuan-Fu(陈远富)†, Wang Ze-Gao(王泽高), Liu Jing-Bo(刘竞博), He Jia-Rui(贺加瑞), and Li Yan-Rong(李言荣)

State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, *China*

(Received 18 February 2013; revised manuscript received 27 February 2013)

Photoelectrical response characteristics of epitaxial graphene (EG) films on Si- and C-terminated 6H-SiC, and transferred chemical vapor deposition (CVD) graphene films on Si-terminated 6H-SiC have been investigated. The results show that upon illumination by a xenon lamp, the photocurrent of EG grown on Si-terminated SiC significantly increases by 147.6%, while the photocurrents of EG grown on C-terminated SiC, and transferred CVD graphene on Si-terminated SiC slightly decrease by 0.5% and 2.7%, respectively. The interfacial buffer layer between EG and Si-terminated 6H-SiC is responsible for the significant photoelectrical response of EG. Its strong photoelectrical response makes it promising for optoelectronic applications.

Keywords: epitaxial graphene, photoelectrical response, oxygen absorption

PACS: 68.65.Pq, 73.40.Lq, 78.67.Wj **DOI:** 10.1088/1674-1056/22/7/076804

1. Introduction

Graphene, as a monolayer to a few layers of sp^2-bonded hexagonally coordinated carbon atoms,[1] has received much attention due to its two-dimensional planar structure and numerous novel properties such as its fast charge transport, quantum-spin Hall effect, suppression of weak localization, transparent and conductive properties.[2–7] Generally, graphene exhibits weak photoresponsive characteristics[8,9] due to its zero-gap band structure.[10,11] Therefore, graphene–based photodetectors are usually prepared in the form of graphene–metal contacts[12] and graphene p–n junctions.[13] In this paper, the photoresponse characteristics of epitaxial graphene grown on Si-terminated 6H-SiC substrate (hereinafter abbreviated to EG-Si), epitaxial graphene grown on C-terminated 6H-SiC substrate (hereinafter abbreviated to EG-C), and transferred chemical vapor deposition (CVD) graphene on Si-terminated 6H-SiC substrate (hereinafter abbreviated to TG-Si) are investigated. It is shown that EG-C and TG-Si show very weak photoresponse ($< 3\%$). However, the EG-Si exhibits a far different photoelectrical response behavior, and its photocurrent-change ratio reaches as large as $\sim 150\%$ upon illumination. The possible mechanism of the photoelectrical response of EG-Si, EG-C, and TG-Si is discussed.

2. Experimental details

The EG-Si and EG-C samples were directly grown on 5×5 mm^2 silicon- and carbon-terminated semi-insulating 6H-SiC substrates, respectively.[14–17] In the preparation of TG-Si sample, we first prepared monolayer graphene on Cu foil by CVD, followed by transferring the monolayer graphene[18,19] onto Si-terminated 6H-SiC substrates. X-ray photoelectron spectroscopy (XPS) was used to characterize the thickness of EG-Si and EG-C. Raman spectroscopy was used to identify the thickness of TG-Si.

The Hall effects of EG-Si, EG-C, and TG-Si were measured by using a van der Pauw configuration with a size of 5×5 mm^2. The graphene samples for photoelectrical response measurements were prepared as follows. Firstly, 200-nm Pt fork electrode was deposited onto graphene film by electron beam evaporation using a shadow mask. Then, the sample was wire bonded to a PCB board, as shown in Fig. 2(a). Finally, the current–voltage (I–V) characteristics were performed by using a Keithley 2000 Multimeter and Yokogawa 7651 Programmable DC voltage source, and the time-dependent photoresponse was measured in a darkroom at room temperature. The simulated sunlight with a power density of 100 mW/cm^2 was used as the light-illumination source which was produced by a spherical short-arc xenon lamp.

*Project supported by the Program for New Century Excellent Talents in University of Ministry of Education of China (Grant No. NCET-10-0291) and the Startup Research Project of University of Electronic Science and Technology of China (Grant No. Y02002010301041).

†Corresponding author. E-mail: yfchen@uestc.edu.cn

© 2013 Chinese Physical Society and IOP Publishing Ltd

3. Results and discussion

The C1s XPS spectra of EG-Si and EG-C are shown in Figs. 1(a) and 1(b), from which one can determine that the thicknesses of EG-Si and EG-C are monolayer and six layers, respectively.[20,21] In addition, the spectrum in Fig. 1(a) can be fitted to four different components: SiC and G peaks represent the bulk SiC and epitaxial graphene layer, respectively; S_1 and S_2 peaks indicate the presentation of $6\sqrt{3}\times 6\sqrt{3}$R30° reconstructed interface buffer layer.[22] It is noted that the electronic property of epitaxial graphene layer can be remarkably affected by the buffer layer and the n-doping feature of graphene caused by the buffer layer has been reported.[23–25] Figure 1(c) shows the Raman spectrum of TG-Si. It is difficult to identify the thickness of the transferred CVD graphene on Si-terminated 6H-SiC substrate, because the G peak of grapheme overlaps with the SiC peak. We also measured the Raman spectroscopy of transferred CVD graphene on SiO_2/Si substrate. As shown by the inset of Fig. 1(c), it is clear that the CVD graphene film is monolayer with high quality.

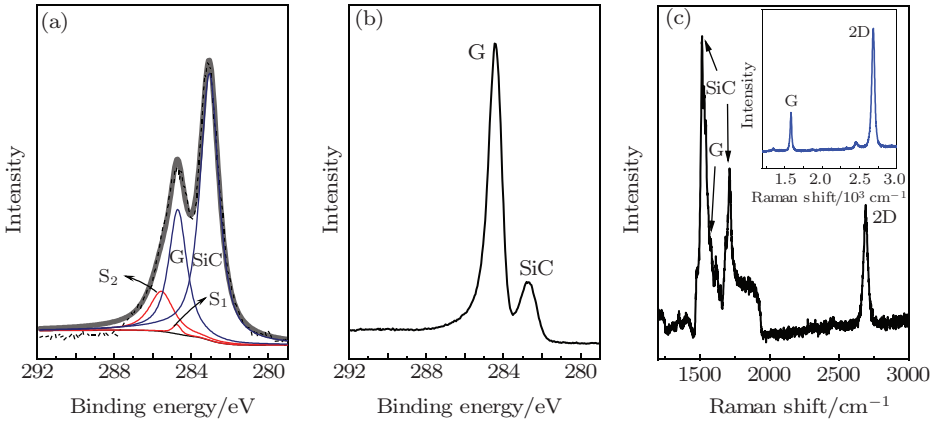


Fig. 1. (color online) (a) C1s XPS spectrum of epitaxial graphene grown on Si-terminated 6H-SiC. The spectrum is fitted to four components which represent a bulk SiC peak (SiC), monolayer layer graphene (G), and interfacial buffer layer (S_1, S_2), respectively. (b) C1s XPS spectrum of epitaxial graphene grown on C-terminated 6H-SiC. (c) Raman spectrum of CVD graphene transferred onto Si-terminated 6H-SiC. Inset: Raman spectrum of CVD graphene transferred onto SiO_2/Si.

Figures 2(b)–2(d) show the *I*–*V* characteristic of EG-Si, EG-C, and TG-Si, respectively. All *I*–*V* curves with illumination on and off exhibit good linearity, which suggests that a good ohmic contact between the Pt fork electrode and the graphene layer was obtained. It is noted that compared to EG-C and TG-Si, the variation of photocurrent with illumination on and off is much more remarkable, which suggests that it has a much stronger photoelectrical response.

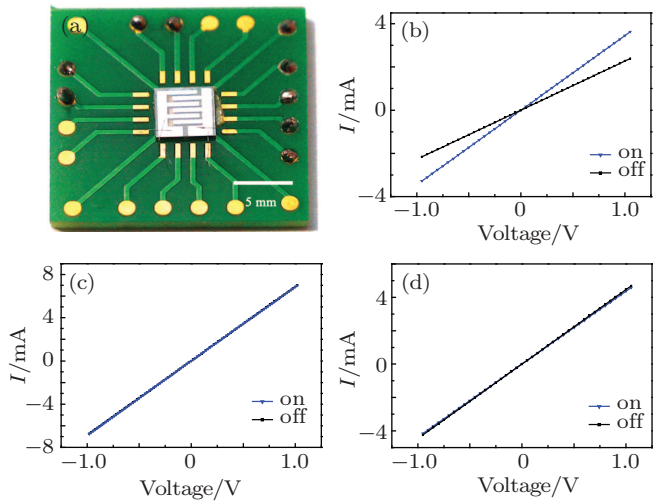


Fig. 2. (color online) (a) Photograph of the graphene sample with a fork electrode for photoelectrical measurements. The *I*–*V* characteristic of (b) EG-Si, (c) EG-C, and (d) TG-Si under dark conditions or exposure to a xenon lamp.

In order to investigate the dynamic photoresponse process, the time-dependent photocurrent was recorded at a fixed bias of 0.1∼V. The time constants of the excitation and decay processes can be extracted by fitting the experimental *I*–*t* curve using the following exponential function:

$$I = A\mathrm{e}^{-t/\tau_r} + I_\mathrm{s}. \tag{1}$$

Figures 3(a)–3(c) show the experimental and simulated *I*–*t* curves of EG-Si, EG-C, and TG-Si, respectively. It is noted that the photoresponse characteristic of EG-Si is very different from those of EG-C and TG-Si. (i) With illumination on (off), the photocurrent of EG-Si increases (decreases), while photocurrents of EG-C and TG-Si decrease (increase), suggesting a completely contrary change tendency. (ii) The change ratio of the photocurrent for EG-Si upon illumination is as large as 147.6%, while corresponding values are only 0.5% and 2.7% for EG-C and TG-Si, which implies that the EG-Si is much more sensitive to the illumination of Xenon lamp. (iii) The time constant of excitation process of EG-Si (30.2 s) is much shorter than those of EG-C (134.2 s) and TG-Si (208.3 s), while the time constant of decay process of EG-Si (3834.2 s) is much longer than that of EG-C (147.0 s) and TG-Si (1399.4 s), indicating completely different excitation and decay processes. Obviously, monolayer graphene, SiC substrate, and the epitaxial growth method are

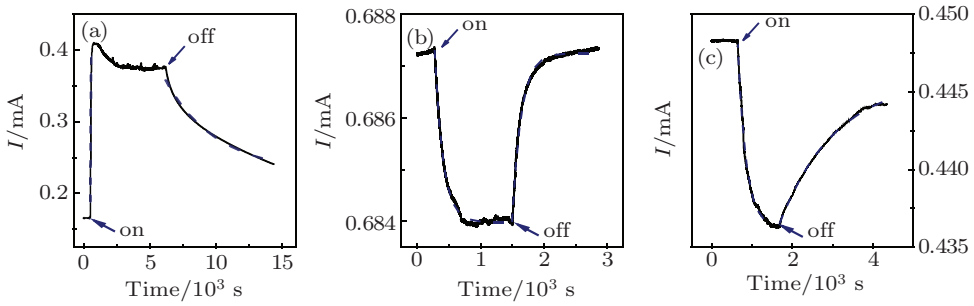


Fig. 3. Time-dependent photoelectrical response of (a) EG-Si, (b) EG-C, and (c) TG-Si. The dashed lines represent corresponding fitted data.

not the key factors causing the significant differences mentioned above. We think that the interfacial buffer layer might be the key reason because there is an interfacial buffer layer in EG-Si, while no buffer layer in EG-C and TG-Si. Detailed discussion is given below.

It is known that due to the interfacial buffer layer, an intrinsic electron (n-type) doping is observed in the epitaxial graphene on Si-terminated SiC substrate.[26] Generally, epitaxial graphene on C-terminated SiC is usually p-type in the air due to oxygen absorption,[27] and transferred CVD graphene is p-type in the air due to residue poly methylmethacrylate (PMMA) doping during the wet-transfer process[28] and adsorption of oxygen and other molecules.[29,30] Our Hall effect measurements show that EG-Si is indeed heavily n-type doped with an electron concentration of 4.94×10^{13} cm^{-2}, while EG-C and TG-Si are indeed p-type with hole concentrations of 2.15×10^{12} and 9.25×10^{12} cm^{-2}, respectively. Thus, now it is not difficult to understand why the change tendency of photocurrent for EG-Si is contrary to that for EG-C and TG-Si. In detail, when n-type EG-Si is illuminated, the oxygen desorption will increase the number of photo-induced electrons, which will increase the total conductive carriers upon illumination, resulting in the increase in photocurrent. However, when p-type EG-C and TG-Si are illuminated, the total conductive carriers decrease, resulting in the decrease in photocurrent.

Theoretical and experimental studies[31,32] have shown that compared to buffer-layer free graphene, EG-Si demonstrates different structure and electronic properties due to the existence of interfacial buffer layer. Based on previous reports, here we present a simple oxygen desorption/absorption model with illumination on/off to roughly analyze how the interfacial buffer layer of EG-Si causes such a different response characteristic. Figures 4(a) and 4(c) show schematics of oxygen absorption for buffer-layer free TG-Si, and EG-Si with interfacial buffer layer, respectively. It is noted that the EG-C is very similar to that of TG-Si except for multi-layer graphene. For TG-Si, oxygen (or other) molecules can be only absorbed by graphene layers, as shown in Fig. 4(a). However, for EG-Si, due to the existence of interfacial buffer layer, oxygen (or other) molecules cannot only be absorbed by graphene layers, but also by the dangling bonds of Si atoms which are not bonded to the C atoms of the interfacial buffer layers, as shown

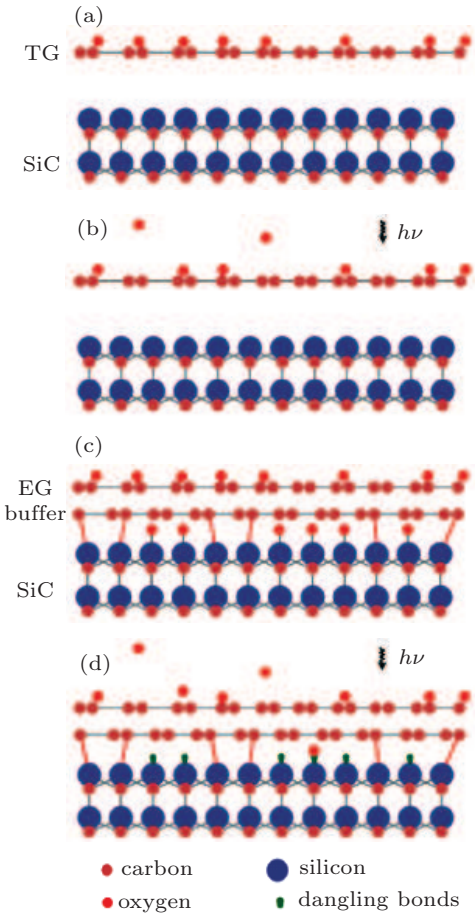


Fig. 4. (color online) Schematic of oxygen absorption/desorption process: oxygen adsorption for TG-Si (a) and EG-Si (c); oxygen desorption upon illumination for TG-Si (b) and EG-Si (d). "TG" denotes transferred CVD graphene, "EG" epitaxial graphene, and "Buffer" $6\sqrt{3}\times6\sqrt{3}$R30° reconstructed interface buffer layer.

in Fig. 4(c). It means that the EG-Si has many more absorption/desorption sites due to the existence of interfacial buffer layer compared to that of buffer-layer free TG-Si. Upon illumination, the absorbed oxygen (other) molecules by graphene layer and interfacial buffer layer will be desorbed, as shown in Figs. 4(b) and 4(d), which will increase the number of photo-induced electrons, resulting in the change of photocurrent. Many more desorption sites and intrinsic heavily n-type lead

to a significant increase in photocurrent of EG-Si upon illumination, as shown in Fig. 3(a). However, when EG-C or TG-Si is illuminated, the current does not decrease so significantly because it has a p-type feature and less desorption sites, as shown in Figs. 3(b) and 3(c). At present, it is still unclear why the photocurrent of EG-Si reaches a maximum quickly, then decreases a little, and finally tends to be saturated upon illumination, as shown in Fig. 3(a). The longer decay time constant for EG-Si relative to that for the EG-C or TG-Si shown in Fig. 3 can be simply explained as follows. It is supposed that it will take much more time for the oxygen (or other) molecules to be absorbed to the interfacial buffer layer than that to be absorbed to graphene layer.

4. Conclusions

In summary, the photoelectrical response characteristics of EG-Si, EG-C, and TG-Si were investigated. Time-dependent photoelectrical results show that upon illumination, the photocurrent of EG-Si significantly increases by 147.6%, while the photocurrents of EG-C and TG-Si slightly decrease by 0.5% and 2.7%, respectively. In addition, for EG-Si, the time constant of excitation is much shorter, while the time constant of decay is much larger than those of EG-C and TG-Si. The huge difference in the photoresponse characteristic of EG-Si may be attributed to the interfacial buffer layer of EG-Si. Strong photoelectrical response makes it promising for potential optoelectronic applications.

References

[1] 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

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

[3] Pisana S, Lazzeri M, Casiraghi C, Novoselov K S, Geim A K, Ferrari A C and Mauri F 2007 *Nature Mater.* **6** 198

[4] 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

[5] Wang X, Zhi L J and Möulen K 2008 *Nano Lett.* **8** 323

[6] Bae S, Kim H, Lee Y B, Xu X F, Park J S, Zheng Y, Balakrishnan J, Lei T, Kim H R, Song Y I, Kim Y J, Kim K S, Ożyilmaz B, Ahn J H, Hong B H and Iijima S 2010 *Nature Nanotechnol.* **5** 574

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

[8] Shi Y, Fang W, Zhang K, Zhang W and Li L J 2009 *Small* **5** 17

[9] Kim M, Safron N S, Huang C, Arnold M S and Gopalan P 2012 *Nano Lett.* **12** 182

[10] Meric I, Han M Y, Young A F, Ozyilmaz B, Kim P and Shepard K L 2008 *Nature Nanotechnol.* **3** 654

[11] Zhou S Y, Gweon G H, Fedorov A V, First P N, de Heer W A, Lee D H, Guinea F, Castro Neto A H and Lanzara A 2007 *Nature Mater.* **6** 770

[12] Xu X D, Gabor N M, Alden J S, van der Zande A M and McEuen P L 2010 *Nano Lett.* **10** 562

[13] Song J C W, Rudner M S, Marcus C M and Levitov L S 2011 *Nano Lett.* **11** 4688

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

[16] Hao X, Chen Y F, Li P J, Wang Z G, Liu J B, He J R, Fan R, Sun J R, Zhang W L and Li Y R 2012 *Chin. Phys. B* **21** 046801

[17] Wang D C, Zhang Y M, Zhang Y M, Lei T M, Guo H, Wang Y H, Tang X Y and Wang H 2012 *Chin. Phys. B* **21** 038102

[18] Li X S, Cai W W, An J, Kim S, 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

[19] Wang Z G, Chen Y F, Li P J, Hao X, Fu Y, Chen K, Huang L X and Liu D 2012 *Vacuum* **86** 895

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

[21] Briggs D and Seah M P 1994 *Practical Surface Analysis: Auger and X-Ray Photoelectron Spectroscopy* (Singapore: John Wiley & Sons) p. 357

[22] Ostler M, Speck F, Gick M and Seyller T 2010 *Phys. Status Solidi (b)* **247** 2924

[23] Walter A L, Jeon K J, Bostwick A, Speck F, Ostler M, Seyller T, Moreschini L, Kim Y S, Chang Y J, Horn K and Rotenberg E 2011 *Appl. Phys. Lett.* **98** 184102

[24] Riedl C, Coletti C, Iwasaki T, Zakharov A A and Starke U 2009 *Phys. Rev. Lett.* **103** 246804

[25] Varchon F, Mallet P, Veuillen J Y and Magaud L 2008 *Phys. Rev. B* **77** 235412

[26] Bostwick A, Ohta T, Seyller T, Horn K and Rotenberg E 2007 *Nature Phys.* **3** 36

[27] Sidorov A N, Gaskill K, Nardelli M B, Tedesco J L, Myers-Ward R L, Jr. Eddy C R, Jayasekera T, Kim K W, Jayasingha R, Sherehiy A, Stallard R and Sumanasekera G U 2012 *J. Appl. Phys.* **111** 113706

[28] Moser J, Barreiro A and Bachtold A 2007 *Appl. Phys. Lett.* **91** 163513

[29] Schedin F, Geim A K, Morozov S V, Hill E W, Blake P, Katsnelson M I and Novoselov K S 2007 *Nature Mater.* **6** 652

[30] Fowler J D, Allen M J, Tung V C, Yang Y, Kaner R B and Weiller B H 2009 *ACS Nano* **3** 301

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

[32] Riedl C and Starke U 2007 *Phys. Rev. B* **76** 245406