Thermal annealing effects on graphene/n-Si Schottky junction solar cell: removal of PMMA residues

Yuzuki Ono and Hojin Im*  
Graduate School of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan  
*E-mail: hojin@hirosaki-u.ac.jp

Received February 15, 2023; revised March 15, 2023; accepted April 4, 2023; published online April 26, 2023

Thermal annealing is one of the most effective ways to improve the efficiency of a graphene/n-Si Schottky junction solar cell. Here, its underlying mechanism has been investigated by comparative studies in terms of the removal of polymethyl methacrylate (PMMA) residues, using the J–V characteristics and transient photocurrent and photovoltage measurements. The obtained results have revealed that there are trap states that originate from the PMMA residues and cause the large photocurrent leakage as the intensity of the incident light increases. It is also found that the PMMA residues accelerate deterioration and rapidly invalidate hole doping effects. Such undesirable PMMA residues were effectively removed by the thermal annealing treatments, serving to reduce the photocurrent leakage and increase the stability.

Supplementary material for this article is available online

1. Introduction

The graphene/n-Si Schottky junction has attracted extensive attention for applications of next generation optoelectrical devices such as solar cell, photodetector, and photosensor, utilizing their unique electrical and optical properties. Among them, the graphene/n-Si Schottky junction solar cell (GSSC) has shown remarkable developments. Since the first report in 2010, its power conversion efficiency (PCE) has increased rapidly from ~1.5% to ~15% by successful efforts such as hole doping of graphene, passivation of silicon surface, antireflection coating, etc. However, there are still several issues to overcome toward practical applications. In the fabrication process of GSSC, polymethyl methacrylate (PMMA) has been widely used as a support layer during the transfer of graphene onto a target such as an n-Si substrate. After the transfer process, the PMMA layer has been removed, usually by acetone. However, it has been hard to completely remove PMMA; hence, its residues have caused the degradation of PCE. Thermal annealing treatment has been considered as one of the most useful methods to remove the PMMA residues and performed usually in the forming gas and/or vacuum, enhancing the performance of GSSC. To fully utilize such thermal annealing effects, it is inevitable to understand their underlying mechanism.

Here, we have studied the thermal annealing effects on GSSC by the current density versus the bias voltage (J–V) characteristics and the transient photocurrent and photovoltage (TPC/TPV) measurements, focusing on the removal of the PMMA residues. The obtained experimental results have revealed that there are the trap states originated from the PMMA residues, which cause the retardation of the photocurrent transport and the photocurrent leakage. In addition, the PMMA residues rapidly invalidate the hole doping effects and accelerate the degradation of its performance. In comparison between GSSCs with and without annealing, we observed that the thermal annealing treatments effectively remove such undesirable PMMA residues, reducing the photocurrent leakage, increasing the stability, and persisting the hole doping effects.

2. Experimental methods

2.1. Graphene growth

Graphene was grown on the catalytic substrate of 30 μm thick Cu-foil by the low-pressure CVD (CVD). The Cu-foil was annealed at 980 °C for 1 h with forming gas (H2:Ar = 1:9) at ~2 mbar. Subsequently, the mixed gases of CH4 (5 sccm) and H2 (30 sccm), which are play roles as the precursor and reduction gas, respectively, were introduced into the CVD quartz chamber for 30 min at 980 °C and ~10 mbar, followed by cooling down the chamber by full-open of the CVD furnace. Graphene was transferred to a target substrate by using the conventional PMMA assisted method. PMMA was spin-coated on the graphene/Cu-foil layer at 3000 rpm for 60 s, and was cured at 80 °C for 10 min. After the removal of graphene grown on the backside of Cu-foil by HNO3 (10 wt%) etching for 1 h, Cu-foil was completely etched off by a FeCl3 solution of 2.5 wt% for 3 h.

2.2. GSSC fabrication

n-type (100) Si wafer of approximately 11 × 11 mm2 size, 200 μm thickness, and 1–10 Ω with thermal SiO2 layers (~500 nm) in both the front and back sides was used as a device substrate. The active area was defined as a window of 3 × 3 mm2 by photolithography. After that, the thermal oxide layers were removed using buffered oxide etchant for 20 min, followed by a cleaning process with acetone, isopropyl alcohol, deionized water, and dry nitrogen gas. Prior to the transfer process, dilute HF (1 wt%) treatments were additionally carried out for 1 min, followed by exposure to air for 2 h to form a native oxide layer for the passivation of the n-Si surface. PMMA/graphene was transferred onto the patterned n-Si substrate by the conventional fishing method. In this work, we have prepared two types of GSSCs. One type is a solar cell where the PMMA layer was removed by the acetone for 90 min. In the other type of device, the PMMA residue was additionally removed by thermal annealing treatment in forming gas (H2:Ar = 1:9) at ~420 °C at ~0.1 atm. Finally, the solar cells have been completed by forming the back ohmic contact by GaIn eutectic and the front contact by silver paste. The front contact has a width of approximately 1 mm and a thickness of less than 1 mm.
2.3. Characterization

The $J$–$V$ characteristics were measured using a source meter (Keithley 2400, Tektronix) in the dark and under illumination. We used a xenon lamp with an AM1.5 G filter as the light source of 1 Sun (100 mW cm$^{-2}$). In low-light intensity dependent measurements, a halogen lamp (MegaLight100, Schott) was employed. The solar cells have been entirely illuminated. The light intensity was adjusted by a NIST traceable calibrated Si-photodetector (FDS1010, Thorlabs). The sheet resistances of the graphene on the SiO$_2$ (300 nm)/n-Si substrate were obtained using the four-point probe method (Keithley 2400, Tektronix). The TPC and TPV responses were obtained using a laser diode of 639 nm (HL6358MG, Thorlabs) and an oscilloscope (MSO5354, Rigol). External quantum efficiency (EQE) was measured by home-built equipment with a monochromator (CS260, Newport) and lock-in amplifier (LI5640, NF) using the halogen lamp. Raman spectra were obtained using a confocal micro-Raman spectrometer with a 532 nm laser (NRS-5100, JASCO).

3. Results and discussion

The top views of the active area of GSSCs without and with the thermal annealing treatment are shown in the left and right panels of Fig. 1(b), respectively. In the without-annealing (wo-a) GSSC, we can observe small white spots with a size of several $\mu$m, which have been considered to mainly come from PMMA residues after removal by acetone.$^{27,30,32}$ On the other hand, in the with annealing (w-a) GSSC, such PMMA residues were effectively eliminated by thermal annealing treatment, even though it is not perfect. These tendencies are reproduced in the graphene transferred on the SiO$_2$/Si substrate, as shown in the photographs in Figs. S1(a) and S1(b). In addition, the Raman spectra before the annealing obviously show the PMMA peaks, $P_1$ around 1450 cm$^{-1}$ and $P_2$ around 2930 cm$^{-1}$, as well as the graphene peaks, $G$ around 1586 cm$^{-1}$ and 2D around 2684 cm$^{-1}$, in the large PMMA residue A [Fig. S1(c)]. After the thermal annealing treatments, the $P_2$ peak disappears, indicating the removal of the PMMA residue, although the change of the $P_1$ peak cannot be analyzed due to the increase of broad band features around 1200–1500 cm$^{-1}$ [Fig. S1(d)]. Such degradation of graphene after the annealing is also observed in the area $B$, where small PMMA residues exist. The broad band has often appeared after the annealing and been considered to come from residual carbons.$^{33}$ We note that the most active area is like an area $B$. This issue should be solved for the high performance of the device.

The dark $J$–$V$ curves of both GSSCs show the excellent rectifying properties, indicating that the Schottky junction is well formed between graphene and the n-Si substrate [Fig. 1(a)].$^{3,4}$ By the analysis based on the thermionic-emission model,$^{34,35}$ the ideality factor ($n$) and the Schottky barrier height (SBH) from the ln $J$ versus $V$ plots were estimated to be 1.3 (1.6) and 0.82 (0.89) eV for the w-a (wo-a) GSSCs, respectively [Fig. 1(c)]. The series resistances ($R_S$) were obtained from the slope of $dV/$d$\ln J$ versus $J$ as shown in Fig. 1(d),$^{21,36–38}$ being 4.7 (7.9) $\Omega$ for the w-a (wo-a) GSSCs, respectively. It is also found that the sheet resistance of the graphene on the SiO$_2$/Si substrate was reduced by $\sim22\%$.

![Fig. 1.](image-url) (a) $J$–$V$ characteristics and (b) photographs of the w-a and wo-a GSSCs. Plots of (c) ln $J$ versus $V$ and (d) $dV/$d$\ln J$ versus $J$, corresponding to the $J$–$V$ characteristics. The solid lines are guide to the eye.
from $\sim 1373$ to $\sim 1077 \, \Omega \, \text{sq}^{-1}$, after thermal annealing. These indicate that the enhancement of the conductivity of graphene plays an important role to improve the Schottky junction properties. Under the illumination of 1 Sun, it is observed that the thermal annealing treatments also change the photovoltaic parameters, the short-circuit current ($J_{SC}$), open-circuit voltage ($V_{OC}$), fill factor (FF), and PCE, from 14.7 mA cm$^{-2}$, 0.47 V, 22%, and 1.5%, to 29.2 mA cm$^{-2}$, 0.41 V, 33%, and 3.9%, respectively. These values are comparable to those of the pristine devices ($PCE = \sim 1.5\%$) in the previous reports.$^{5,11,13}$ In addition, the s-shape feature around $V_{OC}$, observed in wo-a GSSC, disappeared in w-a GSSC. These results mean that the thermal annealing treatments play an effective role to enhance the performance of GSSCs.$^{28}$ The extracted photovoltaic parameters were summarized in Table SI.

To understand the dynamics of the thermal annealing effects, we have performed the TPV and TPC measurements using a square pulse of 639 nm. In Fig. 2(a), it is recognized that the TPV of the wo-a GSSC more slowly decays than that of the w-a GSSC. In general, the relaxation time of TPV has been interpreted as the recombination time of exciton (photoexcited electron–hole pair); hence, the longer relaxation time has a benefit for the efficiency of the solar cell. However, the obtained TPV results show an opposite tendency to the usual interpretation and require a consideration of additional factors. For the detail analysis, we fitted the TPV responses by the double exponential decay equation ($A e^{-t/\tau_1} + B e^{-t/\tau_2}$). The two relaxation times were estimated to be $\tau_1 = 1.1 \times 10^{-4}$ (1.8 $\times$ 10$^{-4}$) s and $\tau_2 = 2.4 \times 10^{-3}$ (4.2 $\times$ 10$^{-3}$) s for the w-a (wo-a) GSSCs, respectively. These values show good agreement with the previous reports, where $\tau_1$ and $\tau_2$ have been considered to come from the interface of the Schottky junction and the Si bulk, respectively.$^{14}$ Although it is difficult to accurately evaluate the $\tau_1$ values due to the short time scale compared to the fitting region, we can recognize that there are not significant changes after the thermal annealing treatments.$^{14}$ On the other hand, the $\tau_2$ value of wo-a GSSC is apparently longer than that of w-a GSSC, as shown in Fig. 2(a). Usually, thermal annealing at $\sim 420^\circ C$ for 3 h is not sufficient to change the Si bulk properties. It is thus reasonable that $\tau_2$ incorporates capacitive effects, originated from the spatial inhomogeneity of the PMMA residue, as well as recombination time in the Si bulk. Therefore, it should be noted that the increase of $\tau_2$ does not simply mean the enhancement of the GSSC performance. For a more accurate understanding of the above TPV decays, complementary experiments, such as an impedance spectroscopy, should be further studied.

Figures 2(b) and 2(c) show the TPC responses of the w-a and wo-a GSSCs in the same time scale to TPV and in the enlarged time scale, respectively. The relaxation time of TPC has been regarded as a charge extraction time. The TPC of w-a GSSC shows a simple exponential decay in a few $\mu$s. This faster decay of TPC, compared to that of TPV, indicates that photogenerated current is effectively collected to the electrodes. On the other hand, in the TPC of wo-a GSSC, it is observed that there is the immediate decay of photocurrent by $\sim 28\%$ at the rising edge, causing the parasite current leakage which is possibly responsible for the low FF and $J_{SC}$ in the J–V characteristics [Fig. 1(a)]. Furthermore, we can observe the shoulder at the falling edge after the light turns off. This behavior indicates that the photogenerated currents are trapped in the PMMA residues, causing the retardation of charge extraction by a few 10 $\mu$s. This decay time is one order of magnitude larger than that of the w-a GSSC and increases the chance of recombination. As a result, we can easily infer that the PMMA residues play a role as recombination sites, deteriorating the performance of GSSCs.

Figure S2 shows the EQE spectra of the w-a and wo-a GSSCs in the range of 350–1100 nm in agreement with the previous reports.$^{9,15}$ Despite the large difference of $J_{SC}$ values in J–V measurements, both GSSCs show the similar spectral feature. When we consider that the EQE spectra are measured using a very weak light intensity compared to the intensity of the 1 Sun, it can be easily inferred that there is a light-intensity dependency in solar cell performance.

To elucidate it, we have investigated the J–V characteristics of the w-a and wo-a GSSCs as a function of the light intensity [Figs. 3(a) and 3(b)]. A halogen lamp, which can continuously adjust the light intensity, was used. The light intensity of the halogen lamp, where $J_{SC}$ has the same value as 1 Sun, was regarded as the 1 Sun-equivalent condition. The variation of $J_{SC}$ and FF were plotted in

![Fig. 2. (a) TPV and (b) TPC responses of the w-a and wo-a GSSCs. (c) Enlarged TPCs near the rising and falling edges, whose times were set to be 0 s. For the sake of comparison, the TPV responses are normalized to each its own maximum intensity, while the TPC responses are raw data.](image-url)
Fig. 3(c). The $J_{SC}$ values of the w-a GSSC are linearly proportional to the light intensity. On the other hand, the $J_{SC}$ values of the wo-a GSSC increase monotonically with the light intensity in the weak light region but start to saturate as the light intensity closes to the 1 Sun-equivalent condition. Similar behaviors are also seen in the variation of FF values, but inversely proportional to the light intensity. In Fig. 3(d), the $\ln J_{SC}$ versus $V_{OC}$ relation of the w-a GSSC shows better linearity than that of the wo-a GSSC, indicating that the Schottky junction of the w-a GSSC is more ideal than that of the wo-a GSSC. These results point out that, as the light intensity closes to the 1 Sun, the photocurrent leakages occur and are larger in the wo-a GSSC than in the w-a GSSC. This also explains why the EQE spectra are similar in the w-a and wo-a GSSCs (Fig. S2). As a result, it is reasonable that the PMMA residues trap photogenerated carriers and deteriorate the performance of GSSC via the photocurrent leakage.

Finally, we investigated the thermal annealing effects on the hole doping of graphene and its ageing in the w-a and wo-a GSSCs. The $J-V$ characteristics of pristine and hole-doped GSSCs have been measured as a function of time [Figs. 4(a) and 4(b)]. Degradation was not observed in the w-a GSSC for 7 d since the fabrication [the inset of Fig. 4(a)], while there was degradation of PCE from 1.5% to 1.2% in the wo-a GSSC [the inset of Fig. 4(b)]. After that, both GSSCs were hole-doped by the evaporation of HNO$_3$ (69 wt%) for 1 min. It is well known that the hole doping of graphene lowers the Fermi level, improving the device performance. The PCE values of the w-a (wo-a) GSSCs were enhanced from 4.0 (1.2) to 7.1 (2.5)% respectively, soon after the hole doping. These values are comparable to those of the hole-doped devices (PCE = $\sim$8.5%) in the previous reports. Usually, the PCE of GSSCs has reached $\sim$15% with the additional treatments such as an antireflection coating, which were not applied in this work to focus on the effects of the PMMA removal via the thermal annealing treatments. The related photovoltaic parameters were summarized in Tables SII–SV. In addition, we recognize that the degradation of the wo-a GSSC is faster than that of the w-a GSSC; PCEs are reduced by $\sim$21 ($\sim$40)% in 1.5 h after the hole doping for w-a (wo-a) GSSCs, respectively, indicating that the PMMA residues accelerate the deterioration of GSSC. In other words, the thermal annealing treatments have effects to enhance the stability as well as PCE by removing the PMMA residues. For reference, the light-intensity dependent $J-V$ characteristics 1 h after the hole doping were also displayed in Fig. S3; the variation of $J_{SC}$ and FF, and $\ln J_{SC}$ versus $V_{OC}$ show the similar behaviors with those of the pristine GSSCs (Fig. 3).

4. Conclusions

In summary, we have investigated the thermal annealing effects on GSSC in terms of the removal of the PMMA residues and elucidated its underlying mechanism by the comparative studies. In TPC measurements, there were the trap states originated from the PMMA residues, which cause the retardation of the photocurrent transport. In TPV measurements, the presence of the PMMA residues could be observed as the increase of the decay time. The light-intensity dependent $J-V$ characteristics revealed that the PMMA residues give rise to the photocurrent leakage, which is a crucial factor to reduce the GSSC efficiency. It is also found that the PMMA residues rapidly invalidate
the hole doping effects and accelerate the deterioration of GSSC. These results were depicted as a schematic illustration and energy diagram in Fig. 5. From the comparison of the w-a and wo-a GSSCs, such undesirable PMMA residues were effectively removed by the thermal annealing treatments, serving to reduce the photocurrent leakage, to increase the stability, and to persist the hole doping effects. We believe that the revealed underlying mechanism of the thermal annealing effects, mainly related to the removal of the PMMA residues, is useful to make a strategy to design and improve GSSC. This also emphasizes an importance of the developments of several methods to effectively remove the PMMA residues.

ORCID iDs

Hojun Im  https://orcid.org/0000-0001-6713-6735

1) K. S. Novoselov, V. I. Fal’ko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim, Nature 490, 192 (2012).
2) F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff, and V. Pellegrini, Sci. 347, 1246501 (2015).
3) A. di Bartolomeo, Phys. Rep. 606, 1 (2016).
4) C. Xie, Y. Wang, Z.-X. Zhang, D. Wang, and L.-B. Luo, Nano Today 19, 41 (2018).
5) S. K. Behura, C. Wang, Y. Wen, and V. Berry, Nat. Photonics 13, 312 (2019).
6) Z. Yin, J. Zhu, Q. He, X. Cao, C. Tan, H. Chen, Q. Yan, and H. Zhang, Adv. Energy Mater. 4, 1300574 (2014).
7) M. F. Bhopal, D. W. Lee, A. ur Rehman, and S. H. Lee, J. Mater. Chem. C 5, 10701 (2017).
8) K. Huang, X. Yu, J. Cong, and D. Yang, Adv. Mater. Interfaces 5, 1801520 (2018).
9) S. Ju, B. Liang, J.-Z. Wang, Y. Shi, and S.-L. Li, Opt. Commun. 428, 258 (2018).
10) T. Mahmoudi, Y. Wang, and Y.-B. Hahn, Nano Energy 47, 51 (2018).
11) X. Kong, L. Zhang, B. Liu, H. Gao, Y. Zhang, H. Yan, and X. Song, RSC Adv. 9, 863 (2019).
12) L. Song, X. Yu, and D. Yang, J. Alloys Compd. 806, 63 (2019).
13) X. Li, H. Zhu, K. Wang, A. Cao, J. Wei, C. Li, Y. Jia, Z. Li, X. Li, and D. Wu, Adv. Mater. 22, 2743 (2010).
14) X. Miao, S. Tongay, M. K. Petterson, K. Berke, A. G. Rinzler, B. R. Appleton, and A. F. Hebard, Nano Lett. 12, 2745 (2012).
15) E. Shi et al., Nano Lett. 13, 1776 (2013).
16) Y. Song, X. Li, C. Mackin, X. Zhang, W. Fang, T. Palacios, H. Zhu, and J. Kong, Nano Lett. 15, 2104 (2015).
17) A. Alnuaimi, I. Almansouri, I. Saadat, and A. Nayfeh, Sol. Energy 164, 174 (2018).
18) L. Lancellotti, E. Bobeico, A. Castaldo, P. Delli Veneri, E. Lago, and N. Lisi, Thin Solid Films 646, 21 (2018).
19) M. A. Rehman, I. Akhtar, W. Choi, K. Akbar, A. Farooq, S. Hussain, M. A. Shelkuld, S. H. Chun, J. Jung, and Y. Seo, Carbon 132, 157 (2018).
20) L. Lancellotti, E. Bobeico, A. Capasso, E. Lago, P. Delli Veneri, E. Leoni, F. Buonocore, and N. Lisi, Sol. Energy 127, 198 (2016).
21) T. Cui et al., J. Mater. Chem. A 1, 5736 (2013).
22) M. Kim et al., Appl. Mater. Today 26, 101267 (2022).
23) R. S. Kim, Y. Zhao, H. Jung, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi, and B. H. Hong, Nature 457, 706 (2009).
24) G. Borin Barin, Y. Song, I. de Fátima Gimenez, A. G. Souza Filho, L. S. Barreto, and J. Kong, Carbon 84, 82 (2015).

Fig. 4. The $J$–$V$ characteristics of the w-a and wo-a GSSCs, hole-doped by the HNO$_3$ evaporation, as a function of time. The insets show the $J$–$V$ curves obtained soon and 7 d after the fabrication of devices before the hole doping.

Fig. 5. (a) Schematic illustration and (b) energy diagram of GSSC with the PMMA residues. SBH and $V_{bi}$ represent SBH and the built-in potential, respectively.

50x160 1) K. S. Novoselov, V. I. Fal’ko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim, Nature 490, 192 (2012).
2) F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A. C. Ferrari, R. S. Ruoff, and V. Pellegrini, Sci. 347, 1246501 (2015).
3) A. di Bartolomeo, Phys. Rep. 606, 1 (2016).
4) C. Xie, Y. Wang, Z.-X. Zhang, D. Wang, and L.-B. Luo, Nano Today 19, 41 (2018).
5) S. K. Behura, C. Wang, Y. Wen, and V. Berry, Nat. Photonics 13, 312 (2019).
25) Y. Chen, X. Gong, and J. Gai, Adv. Sci. 3, 1500343 (2016).
26) Y.-C. Lin, C.-C. Lu, C.-H. Yeh, C. Jin, K. Suenaga, and P.-W. Chiu, Nano Lett. 12, 414 (2012).
27) A. Suhail, K. Islam, B. Li, D. Jenkins, and G. Pan, Appl. Phys. Lett. 110, 183103 (2017).
28) A. Suhail, G. Pan, D. Jenkins, and K. Islam, Carbon 129, 520 (2018).
29) L. Lin et al., Nat. Commun. 10, 1912 (2019).
30) B. Zhuang, S. Li, S. Li, and J. Yin, Carbon 173, 609 (2021).
31) A. Pirkle, J. Chan, A. Venugopal, D. Hinojos, C. W. Magnuson, S. McDonnell, L. Colombo, E. M. Vogel, R. S. Ruoff, and R. M. Wallace, Appl. Phys. Lett. 99, 122108 (2011).
32) H. J. Hwang, Y. Lee, C. Cho, and B. H. Lee, AIP Adv. 8, 105326 (2018).
33) C. Gong et al., J. Phys. Chem. C 117, 23000 (2013).
34) A. G. Martin, Solar Cells: Operating Principles, Technology and System Applications (University of New South Wales, Kensington, 1986).
35) D. Neamen, Semiconductor Physics and Devices: Basic Principles (McGraw-Hill Education, New York, 2012).
36) S. K. Cheung and N. W. Cheung, Appl. Phys. Lett. 49, 85 (1986).
37) M. A. Rehman et al., Carbon 148, 187 (2019).
38) A. Gnisci, G. Faggio, L. Lancellotti, G. Messina, R. Carotenuto, E. Bobeico, P. Delli Veneri, A. Capasso, T. Dikonimos, and N. Lisi, Phys. Status Solidi A 216, 1800555 (2019).