Photocurrent enhancement of graphene phototransistors using p–n junction formed by conventional photolithography process

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A p–n junction was developed in a graphene transistor by a simple photolithography process used in typical semiconductor processes. The p- and n-type regions were formed by coating photoresist on part of the graphene channel and immersion of the uncovered graphene region in alkali developer, respectively. A 3-fold enhancement of the photocurrent was observed at the maximum field effect mobility. It is therefore important to maximize the field effect mobility by doping to maximize the photocurrent. The results obtained here are an important step toward the production of high-sensitivity graphene-based phototransistors compatible with conventional industrial procedures.

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Two-dimensional-based nanomaterials have recently drawn significant attention from both fundamental science and industrial perspectives.¹) Two-dimensional carbon atom-based graphene has a band structure characterized by a zero bandgap and a linear dispersion relation,²,³ which are responsible for its unique electrical and optical properties.⁴) Graphene has rich potential for a wide range of applications, such as transistors,⁵) photodetectors,⁶–⁸) transparent electrodes,¹⁰) biological sensors,¹¹,¹²) and supercapacitors.¹³,¹⁴) Photodetectors are strong candidates for the application of graphene due to their broadband from ultraviolet to terahertz, high-speed operation, and low-cost manufacturing process, which have never been achieved by the present technology. Graphene transistors have been demonstrated to function as simple photodetectors in various wavelength regions.⁶,⁸) However, the optical absorbance of graphene is small at 2.3%; therefore, much research is being conducted toward enhancement of the high sensitivity of graphene-based photodetectors for practical applications.

The photosresponse of graphene includes various mechanisms that include photovoltaic,¹⁵,¹⁶) photothermoelectric,¹⁷) bolometric,¹₈) and photo-gating¹⁹,²⁰) effects.²¹) The photovoltaic effect generates a photo-electromotive force under light irradiation by built-in electric fields at differently doped sections. This effect is exploited in applications such as solar cells. Graphene also exhibits the same photovoltaic effect, which can be increased, and higher sensitivity can be achieved by forming a p–n junction and built-in electric fields for the graphene channel.

Various techniques have been proposed for the formation of p–n junctions in graphene transistors, such as top-gate voltage doping,¹⁶,²²,²³) electron beam irradiation doping,²⁴) and chemical doping.²⁵–²⁷) However, these methods require additional equipment, complicated fabrication procedures, and chemical additives, which is disadvantageous for practical photodetector applications. Therefore, to address this challenge, we have developed a facile method for the fabrication of p–n junction graphene transistors using only a conventional photolithography process. The photolithography process is a technique used to fabricate fine structures for semiconductors using a photoresist and a developer. This method is fundamental for the mass production of electronic and optical devices. If p–n junctions could be formed in graphene with only a conventional photolithography process, then the mass production of graphene photodetectors with high sensitivity could be realized, which would significantly contribute to the advancement of graphene optoelectronic devices.

Figure 1 shows a schematic diagram of the procedure employed for the fabrication of a p–n doped graphene phototransistor. (a) Graphene phototransistors were prepared using p-doped Si substrates. A 290 nm thick SiO₂ layer was thermally formed on the Si substrate. The source/drain electrodes consisted of 10 nm thick Cr and 30 nm thick Au layers formed by vacuum deposition on the SiO₂ layer. (b) Single-layer graphene was fabricated by chemical vapor deposition and transferred onto the source/drain electrodes formed on the SiO₂/Si substrate. (c) The graphene channel (40 µm wide and 40 µm long) was formed using a conventional photolithography process and O₂ plasma etching. The structure of the graphene coating on the electrode can reduce the amount of damage to the graphene caused during the resist removal process in the fabrication of the electrodes. (d) A typical positive-type photoresist (Tokyo Ohka Kogyo OFPR800) was coated on the graphene channel. (e) Some of the photoresist on the graphene channel was removed using a conventional photolithography technique. The sample was then immersed in 2.38 wt % tetramethylammonium hydroxide (TMAH; [(CH₃)₄N]⁺[OH]⁻) solution, which was used as the developer. The sample was then rinsed in pure water, so that most of the TMAH was removed. Finally, two different areas were developed: the area immersed in TMAH and the other area covered by the photoresist without immersion in TMAH. As discussed later, these two areas correspond to n- and p-doped graphene, respectively. The graphene-channel region immersed in the TMAH solution was not covered by a dopant material, a method used in previous studies;²⁶) therefore, there is no attenuation of incident light by the dopant materials.
Three different samples were prepared to investigate the formation of the p–n junction in graphene: sample A with all of the graphene channel immersed in TMAH without photoresist, sample B with all of the graphene channel covered by photoresist, and sample C with the graphene channel partly covered by photoresist and partly immersed in TMAH as shown in the optical micrograph in Fig. 1(f).

The electrical properties of the graphene-based transistors were then measured with the source–drain bias voltage fixed at 0.1 V. Figures 2(a)–2(c) show the source–drain current ($I_d$) as a function of the back-gate voltage ($V_{bg}$) for the A, B, and C samples, respectively. Figure 2(a) shows transfer characteristics for the sample A graphene transistor, and that for a sample that was not immersed in TMAH (pristine sample) for comparison. The Dirac point was clearly shifted to more negative $V_{bg}$ than the pristine sample, which indicates that graphene was successfully doped to n-type by TMAH. TMAH consists of both tetramethylammonium (TMA; [$(CH_3)_4N$]) ions and hydroxide ions (OH). Graphene and TMA are attracted by van der Waals forces in TMAH. TMA is a typical quaternary ammonium ion that releases electrons and becomes a positive ion. Hence, graphene is n-doped by the electrons released from TMA. Figure 2(b) shows the $I_d$–$V_{bg}$ characteristics of the sample B graphene transistor with the photoresist over the entire channel region, and that of a pristine sample without the photoresist for comparison. The Dirac point was shifted to more positive $V_{bg}$ than the pristine sample, which indicates that graphene was doped to p-type. The hole-doping is attributed to the carboxyl group contained in the photoresist as an electron-withdrawing substituent, which is a well-known effect reported in polymethyl methacrylate (PMMA). TMAH and the photoresist can thus act as n- and p-type dopants, respectively. Figure 2(c) shows the transfer characteristics of the p–n junction graphene transistor (sample C). Two Dirac points were formed in both the

![Fig. 1.](image1.png)  
![Fig. 2.](image2.png)
The measured photocurrent included not only that at the p–n junction, which increased the number of photo-carriers generated by the built-in electric fields.

The detailed effect of photocurrent enhancement was investigated. Figures 4(a) and 4(b) show the $V_{bg}$ dependence of $I_d$ and $I_p$, and the mobility of graphene ($\mu$) and $I_p$ with respect to $V_{bg}$, respectively. Here, $\mu$ is the field effect mobility calculated from the transconductance determined from the measurement results in Fig. 4(a). The photocurrent decreased at $V_{bg} > 10$ V, which is attributed to defects in the SiO$_2$ layer formed by thermal oxidation that trap the generated photocarriers. Figure 4(b) shows that $I_p$ has a clear dependence on $\mu$ at $V_{bg} < 10$ V. $\mu$ for the undoped graphene phototransistor was approximately $10^3$ cm$^2$ V$^{-1}$s$^{-1}$, which was increased to approximately $3000$ cm$^2$ V$^{-1}$s$^{-1}$ for the p–n junction graphene phototransistor due to the built-in electric field. The maximum photocurrent was obtained at $V_{bg} = -10$ V, which gives the maximum $\mu$. However, this point is not located in the p+n region, where the potential difference of the p and n region is maximum, as demonstrated in Refs. 15 and 25. In the present experiments, the incident light irradiated the entire graphene channel region, considering the practical applications of graphene-based phototransistors. The measured photocurrent included not only that at the p–n junction interface but also that at the other channel region, including the metal graphene interface. Therefore, these results indicate that the photocurrent is determined by $\mu$ with consideration of the entire graphene channel region being irradiated. The maximum $\mu$ should be located at $V_{bg} = 0$ V.

Fig. 3. (Color online) (a) Back-gate voltage dependence of $I_d$ for the p–n junction and pristine graphene phototransistors. The LED power for all measurements was 20 mW. (b) $I_p$ as a function of time with a bias voltage $V_d$ of 0.1 V in the dark and illuminated states during the measurement with $V_{bg} = -10$ V.

Fig. 4. (Color online) (a) Back-gate voltage dependence of $I_d$ and $I_p$ for the p–n junction graphene phototransistor. (b) Back-gate voltage dependence of the mobility ($\mu$) and $I_p$ for the p–n junction graphene phototransistor.
because the influence of the depletion layer of the p-doped Si substrate increases according to the increase of $-V_{bg}$, which decreases $\mu$. The p–n junction formed in the present graphene phototransistor satisfied this condition by the effect of p–n doping.

In summary, a simple method is proposed for the formation of p–n junctions in graphene transistors using a photolithography process compatible with conventional semiconductor processes. Graphene can be doped to n-type by immersion in a developer (TMAH) and doped to p-type by coating with photoresist. Therefore, p- and n-type regions can be simultaneously fabricated in the graphene channel region using a simple photolithography procedure. The electrical characteristics and photoresponses of p-, n-, and p–n-type phototransistors were measured. The p- and n-type Dirac points were observed and a three-fold photocurrent enhancement was achieved for the p–n junction graphene transistor with respect to the non-doped graphene phototransistor. An enhancement of the photocurrent is obtained at the maximum $\mu$. Thus, it is important to maximize the field effect mobility by doping to maximize the photocurrent. This work is expected to contribute to the realization of low-cost and mass-produced high-sensitivity graphene-based photodetectors.

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1) K. S. Novoselov, V. I. Fal’ko, L. Colombo, P. R. Gellert, M. G. Schwab, and K. Kim, Nature 490, 192 (2012).
2) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, Science 306, 666 (2004).
3) K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos, and A. A. Firsov, Nature 438, 197 (2005).
4) F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, Nat. Photonics 4, 611 (2010).
5) F. Schwierz, Nat. Nanotechnol. 5, 487 (2010).
6) F. Xia, T. Mueller, Y. M. Lin, A. Valdes-Garcia, and P. Avouris, Nat. Nanotechnol. 4, 839 (2009).
7) T. Mueller, F. Xia, and P. Avouris, Nat. Photonics 4, 297 (2010).
8) X. Cai, A. B. Sushkov, R. J. Suess, M. M. Jadidi, G. S. Jenkins, L. O. Nyakiti, R. L. Myers-Ward, S. Li, J. Yan, D. K. Gaskell, T. E. Murphy, H. D. Drew, and M. S. Fuhrer, Nat. Nanotechnol. 9, 814 (2014).
9) S. Ogawa, D. Fujisawa, and M. Ueno, AIP Adv. 3, 112127 (2013).
10) K. S. Kim, Y. Zhao, H. Jang, 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).
11) B. Zhang and T. Cui, Sens. Actuators A 177, 110 (2012).
12) S. Okuda, T. Ikuta, Y. Kanai, T. Ono, S. Ogawa, D. Fujisawa, M. Shimatani, K. Inoue, K. Maehashi, and K. Matsumoto, Appl. Phys. Express 9, 045104 (2016).
13) M. D. Stoller, S. Park, Y. Zhu, J. An, and R. S. Ruoff, Nano Lett. 8, 3498 (2008).
14) Y. Xu, Z. Lin, X. Huang, Y. Liu, Y. Huang, and X. Duan, ACS Nano 7, 4042 (2013).
15) E. C. Peters, E. J. H. Lee, M. Burghard, and K. Kern, Appl. Phys. Lett. 97, 193102 (2010).
16) N. M. Gabor, J. C. W. Song, Q. Ma, N. L. Nair, T. Taychatanapat, K. Watanabe, T. Taniguchi, L. S. Levitov, and P. Jarillo-Herrero, Science 334, 648 (2011).
17) T. J. Echtermeyer, P. S. Nene, M. Trushin, R. V. Gorbachev, A. L. Eiden, S. Milana, Z. Sun, J. Schillernann, E. Lidorikis, K. S. Novoselov, and A. C. Ferrari, Nano Lett. 14, 3733 (2014).
18) J. Yan, M. H. Kim, J. A. Elle, A. B. Sushkov, G. S. Jenkins, H. M. Milchberg, M. S. Fuhrer, and H. D. Drew, Nat. Nanotechnol. 7, 472 (2012).
19) G. Konstantatos, M. Badioli, L. Gauldreaux, J. Osmond, M. Bernechea, F. P. Garcia de Arquer, F. Gatti, and F. H. Koppen, Nat. Nanotechnol. 7, 363 (2012).
20) M. Shimatani, S. Ogawa, D. Fujisawa, S. Okuda, Y. Kanai, T. Ono, and K. Matsumoto, AIP Adv. 6, 035113 (2016).
21) F. H. Koppen, T. Mueller, P. Avouris, A. C. Ferrari, M. S. Vitiello, and M. Polini, Nat. Nanotechnol. 9, 780 (2014).
22) M. C. Lemme, F. H. Koppen, A. L. Falk, M. S. Rudner, H. Park, L. S. Levitov, and C. M. Marcus, Nano Lett. 11, 4134 (2011).
23) J. Liu, S. Safavi-Naeini, and D. Ban, Electron. Lett. 50, 1724 (2014).
24) X. Yu, Y. Shen, T. Liu, T. T. Wu, and Q. Jie Wang, Sci. Rep. 5, 12014 (2015).
25) S. Wang, Y. Sekine, S. Suzuki, F. Maeda, and H. Hino, Nanotechnology 26, 385203 (2015).
26) N. Liu, H. Tian, G. Schwartz, J. B. Tok, T. L. Ren, and Z. Bao, Nano Lett. 14, 3702 (2014).
27) H.-C. Cheng, R.-J. Shiue, C.-C. Tsai, W.-H. Wang, and Y.-T. Chen, ACS Nano 5, 2051 (2011).
28) 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).