Gate Tuning of High-Performance InSe-Based Photodetectors Using Graphene Electrodes

Wengang Luo, Yufei Cao, Pingan Hu, Kaiming Cai, Qi Feng, Faguang Yan, Tengfei Yan, Xinhui Zhang, and Kaiyou Wang*

In order to increase the response speed of the InSe-based photodetector with high photoresponsivity, graphene is used as the transparent electrodes to modify the difference of the work function between the electrodes and the InSe. As expected, the response speed of InSe/graphene photodetectors is down to 120 µs, which is about 40 times faster than that of an InSe/metal device. It can also be tuned by the back-gate voltage from 310 µs down to 100 µs. With the high response speed, the photoresponsivity can reach as high as 60 A W\(^{-1}\) simultaneously. Meanwhile the InSe/graphene photodetectors possess a broad spectral range at 400–1000 nm. The design of 2D crystal/graphene electrical contacts can be important for high-performance optoelectronic devices.

1. Introduction

Developing novel photodetectors is extremely important in the progress of the optoelectronics field. Among a crowd of various photodetectors, 2D-material-based photodetectors are very attractive because of their unique dimensional dependent properties. Graphene, being the first prototype of 2D crystals as the channel material in photodetectors, can offer a broad spectral detection and ultrafast sensing due to its linear energy dispersion and high mobility.\(^{[1–3]}\) However, the intrinsically weak absorption and small built-in potential in these graphene-based photodetectors have severely limited their photoresponsivity down to \(5 \times 10^{-4}\) A W\(^{-1}\) and their external quantum efficiency (EQE) to the range of \(≈0.1–1\%\).\(^{[4]}\) Beyond graphene, novel 2D layered semiconducting materials such as transition metal dichalcogenides (TMDCs) and several III–VI layered materials have attracted considerable attention in optoelectronics due to the finite bandgaps.\(^{[5–7]}\) Among the III–VI layered materials, bulk layered InSe has a narrower direct bandgap (\(E_g = 1.3\) eV) compared with the bandgap of GaS (\(E_g = 3.05\) eV) and GaSe (\(E_g = 2.1\) eV),\(^{[8,9]}\) which overlaps well with the solar spectrum, thus offering a broader spectral response than GaS- and GaSe-based photodetectors.

Recently, InSe-based photodetectors have been reported; one work found that the photoresponsivity of InSe-based photodetectors can reach 12 A W\(^{-1}\), but its response time is only 50 ms.\(^{[10]}\) Another work reported a fast response speed (\(≈488\) µs); however, the responsivity was just \(34.7 \times 10^{-3}\) A W\(^{-1}\).\(^{[11]}\) Obtaining high photoresponsivity and fast response speed simultaneously is very important for the application of photodetectors. Thus, it is very important to increase the response speed of 2D material-based photodetectors with high photoresponsivity. Graphene-based artificial heterostructures (stacking of graphene with other layered materials) are used to increase the photoresponsivity of the 2D material-based photodetectors.\(^{[12–17]}\) More recently, the parallel graphene/few-layer InSe conducting heterostructure was used for photodetectors, and it was found that the photoresponse can be as high as 940 A W\(^{-1}\), where the gain photocurrent was mainly from the shift of the Dirac point of the graphene layer. Also, the response time was not been mentioned in these InSe/graphene parallel conducting devices.\(^{[18]}\) In order to exclude the contribution due to direct conductance from the graphene, it is better to design photodetector InSe devices with graphene only working as electrodes. Due to the high mobility of graphene and the close Fermi level between the intrinsic graphene and the InSe, artificial InSe/graphene heterostructures could dramatically increase the response speed of InSe-based photodetectors. In this work, chemical vapor deposition (CVD)-grown p-type-doped graphene was used as transparent electrodes to generate an artificial heterostructure between the graphene and the InSe. For more details about the p-type doping of graphene, refer to the Supporting Information. A built-in electric field between the InSe and the graphene will be generated, which will provide a driving force for the separation of photogenerated electrons and holes. The InSe/graphene (InSe/G) heterostructure photodetector shows a broad spectral range at 400–1000 nm and the photoresponsivity can reach as high as 60 A W\(^{-1}\). The response time of the InSe/G photodetector is down to 128 µs, which is about 40 times faster than that of the...
reference InSe/metal device. It is noteworthy that the response speed of the InSe/G photodetectors can be effectively tuned by the back-gate voltages.

2. Methods

InSe/G photodetectors were fabricated using mechanically exfoliated few-layer InSe nanosheets. For reference, the Ti/Au directly contacted InSe/M photodetector was also fabricated; for more information about the InSe/M device, refer to the Supporting Information. For the InSe/G device, a few layers of InSe were exfoliated first on the Si/SiO₂ substrate; then the CVD graphene microstamps were transferred to both ends of the InSe nanosheet, and metallic contacts were fabricated on top of the graphene microstamps by using standard electron beam lithography, thermal evaporation, and liftoff. The channel length of the InSe/G photodetectors is typically around 16 µm. The schematic illustrations of the InSe/G heterostructure device is presented in Figure 1a. The thickness of the InSe flakes was determined by atomic force microscopy (AFM). The typical thickness used for the sensitive photodetectors in this work is about 30–50 nm. Figure 1d shows an atomic force microscopy (AFM) image of the few-layered InSe; the thickness is about 33 nm.

3. Result and Discussion

The crystal structure of InSe consists of In-Se-Se-In layers as shown in Figure 1b, where each layer has a hexagonal structure. The distance between two neighboring layers is 0.84 nm.²¹ The high-resolution transmission electron microscopy image is shown in Figure 1c, confirming the structure of the InSe/G heterostructure. The lattice constant of InSe along the a- or b-axes is 0.4 nm, which agrees well with the previous results.²² Two different diffraction patterns are shown in the inset of Figure 1c. Both types of the diffraction patterns present a sixfold symmetry, indicating the good crystalline quality and also the hexagonal structure for both the graphene (marked by green dashed line) and the InSe (marked by the red solid line).

Within the wavelength range from 400 to 1000 nm, the photoreponsivity of InSe/G photodetector shows a very good performance (at light power intensity $P = 0.01 \text{ mW cm}^{-2}$, source–drain voltage $V_{ds} = 10 \text{ V}$), as shown in Figure 2a. A well-defined peak is observed at 500 nm, which corresponds to the energy gap of 2.43 eV and is attributed to the optical transitions from $p_x$- and $p_y$-like orbits to the conduction band.¹¹ The photoreponsivity of the InSe/G photodetector as a function of wavelength slowly decreases from $60 \text{ A W}^{-1}$ at $\lambda = 500 \text{ nm}$ to $5.3 \text{ A W}^{-1}$ at $\lambda = 1000 \text{ nm}$.

The $\text{EQE}$, defined as the number ratio of electrons flowing out of the device in response to impinging photons, can be expressed as $\text{EQE} = \frac{h R}{e \lambda}$, where $h$ is Planck’s constant, $c$ is the light velocity, $R$ is the responsivity, $e$ is the elementary electronic charge, and $\lambda$ is the excitation wavelength. As shown in Figure 2a (the red dots), the EQE has the same wavelength dependence on the photoresponsivity spectrum, where the maximum value of the InSe/G photodetector is $\approx 14850\%$. The photoresponsivity of InSe/M photodetector has similar wavelength dependence (refer to the Supporting Information), but it can reach as high as $700 \text{ A W}^{-1}$ at $P = 0.01 \text{ mW cm}^{-2}$, $V_{ds} = 10 \text{ V}$.
Figure 2. a) The photoresponsivity and EQE of InSe/G photodetector as a function of the illumination wavelength; b) typical $I_{ds}$ curves of the InSe/G photodetector with illumination at various excitation intensities (0.01, 0.05, 0.5, 1.5 and 2 mW cm$^{-2}$) at $V_{g} = 0$ V, and the dark current of the InSe/G photodetector; c) photocurrent (blue solid dots) and responsivity (black open squares) as a function of the illumination intensity at $V_{ds} = 10$ V and $V_{g} = 0$ V, the red lines are the fitting curves. d) The 3D responsivity map of the InSe/G photodetector.

Due to the weak light absorption of the graphene, hole–electron pairs are mainly generated from the InSe under illumination, where the photocurrent originates from the swept electrons and holes in different directions under electric fields. To quantitatively analyze the dependence of the illumination intensity upon the photoresponse, the photocurrent ($I_{ph} = I_{ds} - I_{dark}$) as a function of the light intensity $P$ was obtained at fixed source–drain voltage $V_{ds} = 10$ V, as shown in Figure 2c. The photocurrent increases sublinearly following a power law of $I \propto P^{\alpha}$, where $\alpha \approx 0.3$ for the InSe/G device, while $\alpha \approx 0.45$ for the InSe/M device (refer to the Supporting Information). The fitting parameters are much smaller than that of the ideal value of 1.$^{[25]}$ The defects and charged impurities in InSe, InSe/SiO$_2$, and graphene/InSe interface might account for the sublinear power dependence, where more traps could be filled by photoinduced charge carriers with increasing the light intensity, leading to the final saturation of the photocurrent. A similar phenomenon was previously observed in MoS$_2$ photodetectors.$^{[24]}

One critical figure of merit to determine the performance of the photodetector is the photoresponsivity ($R = I_{ph}/P$), which is defined as the ratio of the generated photocurrent ($I_{ph}$) in response to optical power intensity ($S$ is the sample area).$^{[23]}$ The photoresponsivity as a function of illumination power density increases sublinearly, following a power law of $R \propto P^{-\beta}$. As shown in Figure 2c, the photoresponsivity decreases from 60 to 1.57 A W$^{-1}$ with the illumination intensity increase from 0.01 to 2.2 mW cm$^{-2}$. As shown in the 3D photoresponsivity map of Figure 2d, the photoresponsivity can be tuned not only by the illumination intensity but also by the source–drain voltages. The increasing $V_{ds}$ can shorten the carriers’ transit time by providing a stronger electric field to govern the photoinduced carriers reaching the electrodes, thus reducing the possibility of recombination.

The time-dependent photoresponse of the InSe/G photodetector, under global illumination with a light intensity of 2 mW cm$^{-2}$ at different bias voltages, is shown in Figure 3a. The sensitive, fast, and reversible switching between the on and off states allows the device to act as a high-quality photodetector and switcher. The dynamic response to the light illumination for rising and falling in our devices can be expressed by $I(t) = I_0 [1 - \exp(-t/\tau_r)]$ and $I(t) = I_0 \exp(-t/\tau_a)$, respectively, where $\tau_r$ and $\tau_a$ are the time constants for the rising and decay responses, respectively. Comparing the fitted results between the InSe/G heterostructure and InSe/M devices, the rising and falling times of the InSe/G device are much faster than that of the InSe/M device. The photocurrent of the InSe/M device rises dramatically within 4.8 ms after light illumination and the falling time of $\tau_a$ is about 5.6 ms, as shown in Figure 3b, inset. However, for the InSe/G photodetector, the rising and falling times decrease dramatically to 120 and
220 µs (Figure 3b), respectively. To our knowledge, that is superior to all 2D-material-based photodetectors (except graphene photodetectors). Notably, as shown in Figure 3a and Figure S5a (Supporting Information), the falling edge of the photocurrents exhibits two-step relaxation with a rapid fall in the first step (τ_{d1} < 10 ms) and a slow fall in the second step (τ_{d2} > 1 s). This phenomenon was also observed in previous studies. [10,26,27] By fitting the second decaying stage, almost the same long decay time constant (5.83 s for InSe/G and 5.65 s for InSe/M) was obtained (Figure S5b, Supporting Information). The two different time constants in the decaying stage imply the existence of various traps in the sample and the relatively long decay time constant can be attributed to the inherent trap states in InSe nanosheet. A list of the performance metrics for comparison among the recently developed 2D material-based photodetectors is provided in Table S1 (Supporting Information). The very fast response of the InSe-based photodetector suggests that using graphene as transparent electrodes can effectively improve the InSe photodetectors.

In order to investigate the influence of the p-type doping graphene on the InSe photodetector, we explored the dependence of the current profile on the back-gate voltages (V_{gb}) in the InSe/G photodetector. As shown in Figure 4a, at fixed V_{ds} = 10 V and light intensity P = 2.5 mW cm^{-2}, the photocurrent first decreases with sweeping the V_{gb} from ~80 to 40 V, while it increases with increasing V_{gb} further from 40 to 80 V. As shown in Figure 4a (up inset), the dark current also decreases with sweeping the V_{gb} from ~80 to 0 V, and it increases when sweeping V_{gb} from 0 to 40 V, but it decreases with increasing V_{gb} further from 40 to 80 V. This dependence of the dark current on the back-gate voltages results from the difference between the source–drain voltage and the Schottky barriers between the graphene and the InSe nanosheet. (For more information about the dark current at different back-gate voltages, refer to Section 4 of the Supporting Information). Interestingly, the rising time exhibits the same dependence on V_{gb} as that of I_{ph}, which can be tuned from 310 to 100 µs by the V_{gb}, as shown in Figure 4b. The same dependence of the photocurrent and the response time on the back-gate voltages suggests they have the same physical origin. The back-gate voltages can tune the Fermi levels of the graphene and the InSe, which will change the Schottky barrier between the graphene and the InSe nanosheet. When graphene and InSe are in contact, the Fermi levels must coincide at the interface. The work function of intrinsic graphene is about 4.56 eV [28] and the Fermi level of InSe (E_f (InSe)) is about 4.45 eV [29]. Before applying a back-gate voltage, there is an initial built-in potential between the p-type graphene and n-type InSe interface. Under...
illumination, the photogenerated carriers in the InSe/G device can immediately move to the graphene layer due to the built-in electric field and applied electrostatic field. The much smaller Schottky barrier of the InSe/G device and the high mobility of graphene result in a much faster response speed to that of the InSe/M devices.

The mechanism of the back-gate voltages tuning the photocurrent and response speed can be divided into three situations where the Fermi level of graphene (\(E_F\) (G)) is under, equal, and above to that of InSe. When applying a negative back-gate voltage (\(E_F\) (G) < \(E_F\) (InSe)) (left band diagram in Figure 4a), the down-shifted Fermi level of InSe results in a larger energy barrier between the graphene and the conduction band of the InSe. Meanwhile the Fermi level of the graphene is shifted down, leading to more p doping, which will increase the built-in potential between the graphene and the InSe. Therefore, upon illumination, more photogenerated carriers can be separated by the bigger built-in potential, which will result in a relatively large photocurrent. However, the large Schottky barrier will increase the capacitance and the resistance between the graphene and the InSe, which will decrease the response speed. With increasing the back-gate voltages from negative to 40 V, the Schottky barrier between the graphene and the InSe decreases, which results in the increase of the response speed. When \(V_g = 40\) V, the Fermi level of the graphene will be equal to that of the InSe (middle band diagram in Figure 4a), there will be no built-in potential between the InSe and the graphene. When the photocurrent decreases to the minimum value, the response speed increases to the maximum value. Continuing to increase the back-gate voltage further, the Fermi level of graphene will be higher than that of the InSe, so that the opposite Schottky barrier and built-in potential between graphene and InSe are formed again, as shown in the right side band diagram of Figure 4a. Similar to the first case, the Schottky barrier and built-in potential will increase the photocurrent and decrease the response speed. Meanwhile, the Schottky barrier will restrict tunneling and thermionic currents. The measured \(I_{ds}-V_{ds}\) curves of InSe/G at different back-gate voltages proved the correctness of our mechanism (refer to Figure 4 of the Supporting Information). As shown in Figure S6a (Supporting Information), the non-linear \(I_{ds}-V_{ds}\) curves, at \(V_g = -80, -40, 0\), and +80 V, identify the non-Ohmic contacts. Meanwhile, when \(V_g\) equals 40 V, the output curve is almost linear (Figure S6a (inset), Supporting Information), indicating the absence of a built-in potential, thus exhibiting Ohmic behavior. The photoresponse ratio \(I_{light}/I_{dark}\) as shown in the inset of Figure 4b) has the similar dependence of \(V_g\) with that of \(I_{ds}\), and this dependence demonstrates that the Schottky barrier will restrict the tunneling and the thermionic current.

4. Conclusion

In summary, we used graphene as transparent electrodes to fabricate InSe/G photodetectors on SiO\(_2\)/Si substrate and decreased its response time down to 120 µs. The response time can be tuned from 310 µs down to 100 µs by the back-gate voltage, which is about 40 times faster than that of our InSe/M device. Meanwhile, the InSe/G photodetectors have high responsivities over a broad spectral range at 400–1000 nm. The high responsivity (\(R = 60\) A W\(^{-1}\)) and broad spectral response (from visible to near-infrared) are important for wide-spectral photodetectors. Our work suggests that the response speed of a 2D-material photodetector can be improved by using the graphene as electrodes to design heterostructure photodetectors with high photoresponsivity, which could be very important for future integrated optoelectronic applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by “973 Program” (Grant Nos. 2011CB922201 and 2014CB643903) and NSFC (Grant Nos. 61225021 and 11474276).

Received: April 9, 2015
Revised: May 25, 2015
Published online: June 29, 2015
[17] W. Zhang, C. P. Chuu, J. K. Huang, C. H. Chen, M. L. Tsai, Y. H. Chang, C. T. Liang, Y. Z. Chen, Y. L. Chueh, J. H. He, M. Y. Chou, L. J. Li, Sci. Rep. 2013, 4, 3826.
[18] Z. Chen, J. Biscaras, A. Shukla, Nanoscale 2015, 7, 5981.
[19] W. G. Luo, H. F. Wang, K. M. Cai, W. P. Han, P. H. Tan, P. A. Hu, K. Y. Wang, Chin. Phys. Lett. 2014, 31, 067202.
[20] Y. Q. Bie, Y. B. Zhou, Z. M. Liao, K. Yan, S. Liu, Q. Zhao, S. Kumar, H. C. Wu, G. S. Duesberg, G. L. W. Cross, J. Xu, H. Peng, Z. Liu, D. P. Yu, Adv. Mater. 2011, 23, 3938.
[21] C. D. Blasi, G. Micocci, S. Mongelli, A. Tepore, J. Cryst. Growth 1982, 57, 482.
[22] P. Gomes da Costa, R. G. Dandrea, R. F. Wallis, M. Balkanski, Phys. Rev. B 1993, 48, 14135.
[23] Y. F. Cao, K. M. Cai, P. A. Hu, L. X. Zhao, T. F. Yan, W. G. Luo, X. H. Zhang, X. G. Wu, K. Y. Wang, H. Z. Zheng, Sci. Rep. 2015, 5, 8130.
[24] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, A. Kis, Nat. Nanotechnol. 2013, 8, 497.
[25] F. Xia, T. Mueller, R. Golizadeh-Mojarrad, M. Freitag, Y. M. Lin, J. Tsang, V. Perebeinos, P. Avouris, Nano Lett. 2009, 9, 1039.
[26] Y. Jiang, W. J. Zhang, J. S. Jie, X. M. Meng, X. Fan, S. Lee, Adv. Funct. Mater. 2007, 17, 1795.
[27] S. E. Ahn, J. S. Lee, H. Kim, S. Kim, B. H. Kang, K. H. Kim, G. T. Kim, Appl. Phys. Lett. 2004, 84, 5022.
[28] R. Yan, Q. Zhang, W. Li, I. Calizo, T. Shen, C. A. Richter, R. Angela, A. R. Hight-Walker, X. Iang, A. Seabaugh, D. Jena, H. G. Xing, D. J. Gundlach, N. V. Nguyen, Appl. Phys. Lett. 2012, 101, 022105.
[29] M. Di Giulio, G. Micocci, A. Rizzo, A. Tepore, J. Appl. Phys. 1983, 54, 5839.