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Special Focus on Two-Dimensional Materials and Device Applications

# Bi<sub>2</sub>O<sub>2</sub>Se/BP van der Waals heterojunction for high performance broadband photodetector

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**Abstract** Broadband photodetector has wide applications in the field of remote sensing, health monitoring and medical imaging. Two-dimensional (2D) materials with narrow bandgaps have shown enormous potential in broadband photodetection. However, the device performance is often restricted by the high dark currents. Herein, we demonstrate a high performance broadband photodetector by constructing Bi<sub>2</sub>O<sub>2</sub>Se/BP van der Waals heterojunction. The device exhibits a p-n diode behavior with a current rectification ratio of ~20. Benifited from the low dark current of the heterojunction and the effective carrier separation, the device achieves the responsivity (*R*) of ~ 500 A/W, ~ 4.3 A/W and ~ 2.3 A/W at 700 nm, 1310 nm and 1550 nm, respectively. The specific detectivity ( $D^*$ ) is up to ~  $2.8 \times 10^{11}$  Jones (700 nm), ~  $2.4 \times 10^{9}$  Jones (1310 nm) and ~  $1.3 \times 10^{9}$  Jones (1550 nm). Moreover, the response time is ~ 9 ms, which is more than 20 times faster than that of individual BP (~ 190 ms) and Bi<sub>2</sub>O<sub>2</sub>Se (~ 180 ms) devices.

Keywords Bi<sub>2</sub>O<sub>2</sub>Se/BP, van der Waals heterojunction, broadband photodetector, low dark current, narrow bandgap

## 1 Introduction

Photodetectors based on two dimensional (2D) layered semiconductor materials have been widely studied owing to their ultra-thin characteristics, strong light absorption and tunable optoelectronics properties [1,2]. A variety of narrow bandgap 2D semiconductors have been explored for broadband photodetection, such as black phosphorus (BP) [3,4], black arsenic phosphorus (AsP) [5,6] and bismuth oxyselenide (Bi<sub>2</sub>O<sub>2</sub>Se) [7,8]. High responsivity and detectivity have been achieved in these broadband 2D photodetectors. However, these 2D photodetectors with high responsivity are often operated in photoconductive mode, which suffer from high dark current and slow response speed [9,10]. Generally, a good photodetectors needs to have high sensitivity, fast response speed, broadband response and high detectivity, which are rare to meet simultaneously in individual 2D material. Van der Waals (vdW) heterojunction provides an alternative platform to satisfy the requirements above simultaneously [11–13]. The built-in electrical field ( $E_{in}$ ) generated at the junction region can be utilized to suppress dark current and separate the photogenerated electron-hole pairs for fast photoelectric conversion [12–14]. Therefore, constructing vdW heterojunction will help solve the problems of high dark current in narrow bandgap 2D material based photodetector and achieve high performance broadband photodetection.

Herein, we design a vdW heterojunction photodetector based on Bi<sub>2</sub>O<sub>2</sub>Se and BP thin flakes. The Bi<sub>2</sub>O<sub>2</sub>Se/BP heterojunction exhibits a diode behavior with a current rectification ratio of ~ 20. Utilizing the dual absorption and the effective carrier separation, the device demonstrates high responsivity (*R*) of ~500 A/W, ~ 9.5 A/W, ~ 4.3 A/W and ~ 2.3 A/W at 700 nm, 850 nm, 1310 nm, and 1550 nm, respectively. Benefit from the low dark current of the heterojunction, the specific detectivity ( $D^*$ ) under 700 nm illumination reaches ~  $2.8 \times 10^{11}$  Jones, which is two orders of magnitude higher than that of BP

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Figure 1 (Color online) Structural characterizations of  $Bi_2O_2Se/BP$  vdW heterojunction. (a) Schematic of the  $Bi_2O_2Se/BP$  vdW heterojunction photodetector. (b) Raman spectra of BP,  $Bi_2O_2Se$ , and  $Bi_2O_2Se/BP$  heterojunction regions. (c) and (d) Optical and AFM images of the device. The scale bar is 6  $\mu$ m. (e) Height profile of BP and  $Bi_2O_2Se$  flakes corresponding to the white line marked in (d).

 $(\sim 3.0 \times 10^9 \text{ Jones})$  and  $\text{Bi}_2\text{O}_2\text{Se}$  ( $\sim 3.8 \times 10^9 \text{ Jones}$ ) devices. In addition, the fast response speed of  $\sim 9 \text{ ms}$  is achieved, more than 20 times faster than the photodetectors built on BP ( $\sim 190 \text{ ms}$ ) and  $\text{Bi}_2\text{O}_2\text{Se}$  ( $\sim 180 \text{ ms}$ ). This heterojunction photodiode with high performance and broadband photodetection provides an important platform for the application of photodetector.

## 2 Results and discussion

(1) Architecture of Bi<sub>2</sub>O<sub>2</sub>Se/BP vdW heterojunction. Figure 1(a) shows a schematic view of the Bi<sub>2</sub>O<sub>2</sub>Se /BP vdW heterojunction device, constructing by stacking BP thin flake on top of 2D Bi<sub>2</sub>O<sub>2</sub>Se thin flake. 2D Bi<sub>2</sub>O<sub>2</sub>Se flake was synthesized on a mica surface by chemical vapor deposition (CVD) methods and transferred onto a 300 nm SiO<sub>2</sub>/Si substrate by using the PMMA-mediated method (see Figure S1). BP thin flake was then transferred onto the Bi<sub>2</sub>O<sub>2</sub>Se flake using polydimethylsiloxane (PDMS) as the supporting substrate. Thereafter, the 5 nm/50 nm Ni/Au electrodes were patterned using the standard e-beam lithography and deposited using a thermal evaporator. The optical and atomic force microscope (AFM) images of the heterojunction are shown in Figures 1(c) and (d). From the AFM profile (Figure 1(e)), the thicknesses of the Bi<sub>2</sub>O<sub>2</sub>Se and BP layers are ~ 28 nm and ~ 19 nm, respectively. The Raman spectra are collected and shown in Figure 1(b). Three characteristic peaks at ~ 364, ~ 440, and ~ 468 cm<sup>-1</sup> correspond to  $A_g^1$ ,  $B_g^2$ , and  $A_{2g}$  modes of BP thin flake [15], respectively. As for Bi<sub>2</sub>O<sub>2</sub>Se, the characteristic peak,  $A_{1g}$ , at ~ 160 cm<sup>-1</sup> can be observed [16]. In addition, the Raman characteristic peaks of both BP and Bi<sub>2</sub>O<sub>2</sub>Se can be clearly observed in the Bi<sub>2</sub>O<sub>2</sub>Se/BP heterojunction region and no shift was observed compared to the spectra of the individual flakes, signifying good crystal quality of each component in the heterojunction.

(2) Electrical characterizations of Bi<sub>2</sub>O<sub>2</sub>Se/BP vdW heterojunction. Transfer characteristics of the Bi<sub>2</sub>O<sub>2</sub>Se and BP field effect transistors (FET) are shown in Figure 2(a). All the electrical characteristics of the devices were measured under room temperature atmosphere by using a Keithley 2612 analyzer. BP shows a typical p-type behavior [17] and Bi<sub>2</sub>O<sub>2</sub>Se shows a typical n-type behavior [7]. The hole mobility in BP FET is calculated to be ~ 180 cm<sup>2</sup>/Vs and the electron mobility in Bi<sub>2</sub>O<sub>2</sub>Se FET is calculated to be ~ 180 cm<sup>2</sup>/Vs. Output characteristics are also measured and shown in Figure S2. Both devices exhibit almost symmetric  $I_{ds}$ - $V_{ds}$  curves, indicating good contact with the Ni/Au electrodes. With p-type characteristics in BP and n-type characteristics in Bi<sub>2</sub>O<sub>2</sub>Se, the vertically stacked Bi<sub>2</sub>O<sub>2</sub>Se/BP



Figure 2 (Color online) Electrical characterizations of the  $Bi_2O_2Se/BP$  vdW heterojunction. (a) The transfer characteristics of the  $Bi_2O_2Se$  FET and BP FET. (b)  $I_{ds}$ - $V_{ds}$  characteristic of the  $Bi_2O_2Se/BP$  vdW heterojunction. The inset shows the curve plotted on logarithmic scale. (c) Energy band diagram of the BP/Bi\_2O\_2Se vdW heterojunction at equilibrium before and after contact. (d) Energy band diagrams of the  $Bi_2O_2Se/BP$  vdW heterojunction device under different bias voltage  $V_{ds}$ .

heterojunction forms a natural p-n junction [18]. Figure 2(b) shows the  $I_{ds}$ - $V_{ds}$  curve of the Bi<sub>2</sub>O<sub>2</sub>Se/BP p-n junction, where drain bias is applied to the BP. The  $I_{ds} - V_{ds}$  curve reveals a typical p-n diode-like current rectification behavior and possesses a rectification ratio of ~ 20. In addition, the fitted ideality factor of the diode is ~1.24 [19], indicating a high quality heterojunction interface.

According to the previously reported measurements results and first-principles density of states in the literature, the conduction band minimum  $(E_{\rm C})$ , valence band maximum  $(E_{\rm V})$  and Fermi level  $(E_{\rm F})$  of the BP (Bi<sub>2</sub>O<sub>2</sub>Se) locate at ~ -4.2 eV (-4.15 eV), -4.59 eV (-4.95 eV) and -4.5 eV (-4.37 eV), respectively [20–24]. Figure 2(c) describes the predicted energy band diagram of Bi<sub>2</sub>O<sub>2</sub>Se/BP heterojunction at equilibrium before and after contact. The large work function difference leads to the accumulation of holes in Bi<sub>2</sub>O<sub>2</sub>Se and electrons in BP, and forms a natural p-n junction in the device. In order to understand the mechanism of the diode-like rectification observed in the Bi<sub>2</sub>O<sub>2</sub>Se/BP heterojunction, we drew the energy band diagrams under both forward and reverse bias conditions (Figure 2(d)). Under forward bias, the built-in electric field of the heterojunction is compensated by the external electric field, which is beneficial for electrons (majority carriers) transfer from Bi<sub>2</sub>O<sub>2</sub>Se to BP and resulting in an increase in the current. On the other hand, the reverse bias enhances the built-in electric field. It widens the depletion region and increases the potential barrier, which decreases the current and generates the current-rectifying characteristics of the junction [25].

(3) Optoelectronic characteristics of the Bi<sub>2</sub>O<sub>2</sub>Se/BP vdW heterojunction. Figure 3(a) shows the  $I_{ds}$ - $V_{ds}$  curves of the device under dark and 700 nm focused laser illumination with different incident powers. A Chameleon with Compact OPO (Coherent Inc.) was used as light source. With increasing light power, the channel current gradually increases under the negative bias. Figure 3(b) presents the magnified  $I_{ds}$ - $V_{ds}$  curves. The negative short circuit current ( $I_{sc}$ ) and positive open circuit voltage ( $V_{oc}$ ) indicate the photovoltaic effect of the device [19]. The photocurrent,  $I_{ph}$  (defined as  $I_{ph} = I_{light} - I_{dark}$ ), is extracted from the  $I_{ds}$ - $V_{ds}$  curves and plotted in Figure 3(c). Larger  $I_{ph}$  can be obtained under negative bias, demonstrating the higher photoresponse at reverse bias regime. Scanning photocurrent mapping is used to distinguish the photocurrent domain. The photocurrent mapping were conducted using a Witec confocal Raman system with Ar ion laser (532 nm) excitation. As shown in Figure 3(d), a strong photocurrent is observed in the junction area and no obvious photocurrent is observed at bare Bi<sub>2</sub>O<sub>2</sub>Se



Figure 3 (Color online) Photoresponse of the Bi<sub>2</sub>O<sub>2</sub>Se/BP vdW heterojunction. (a) Power depended  $I_{ds}$ - $V_{ds}$  curves under 700 nm laser illumination. The inset is the schematic diagram of the Bi<sub>2</sub>O<sub>2</sub>Se/BP vdW heterojunction based photovoltaic device. (b) The enlarged view of the  $I_{ds}$ - $V_{ds}$  curves in (a). (c) The photocurrent extracted from (b). (d) Scanning photocurrent mapping of the device under 532 nm laser illumination at  $V_{ds} = 0$  V. The scale bar is 10 µm. (e) Energy band diagram of the Bi<sub>2</sub>O<sub>2</sub>Se/BP vdW heterojunction under 700 nm laser illumination at reverse (i), zero (ii), forward (iii) bias.

and BP regions. It unambiguously certifies the photocurrent indeed originates from the Bi<sub>2</sub>O<sub>2</sub>Se/BP heterojunction [10]. To explain the photovoltaic phenomenon, an energy band schematic diagram of the device under light illumination is shown in Figure 3(e). Under illumination, electron-hole pairs are generated in the both Bi<sub>2</sub>O<sub>2</sub>Se and BP. At the junction region, the electrons are driven to Bi<sub>2</sub>O<sub>2</sub>Se while the holes are driven to BP by the built-in electric field, thus resulting in positive  $V_{oc}$  and negative  $I_{sc}$  (Figure 3(b)). When a reverse bias is applied to the device (Figure 3(e-i)), the width of the depletion region and potential barrier increases. It enhances the separation of the carriers and increases the photocurrent. On the contrary, the forward bias compensates the built-in electric field (Figure 3(e-iii)), which narrows the depletion region and decreases the photocurrent [2].

Figure 4(a) shows the power depended responsivity of BP,  $Bi_2O_2Se$  and  $Bi_2O_2Se/BP$  heterojunction under visible light (700 nm) irradiation. All measurements are performed under -1 V bias voltage. The highest R (defined as  $R = \frac{I_{\rm ph}}{P}$ ) of the heterojunction is ~ 500 A/W, which is higher than that of BP (~ 55 A/W), Bi<sub>2</sub>O<sub>2</sub>Se (~ 225 A/W) device.  $D^*$  used to demonstrate the ability of the de-vice to detect minimum illumination signal. By using  $D^* = \frac{\sqrt{SR}}{\sqrt{2eI_{\rm dark}}}$  (S is the area of the device), we have calculated the specific detectivity of  $D^*$ , which is also shown in Figure 4(b). Because of the low dark current of the heterojunction (Figure S2), the  $D^*$  of the Bi<sub>2</sub>O<sub>2</sub>Se/BP device is up to ~ 2.8  $\times$  10<sup>11</sup> Jones, which is nearly two orders of magnitude higher than that of individual BP ( $\sim$  3.0  $\times 10^9$  Jones) and Bi<sub>2</sub>O<sub>2</sub>Se devices (~ 3.8 × 10<sup>9</sup> Jones). Figure 4(c) shows the photo-switching characteristics. The response times of  $Bi_2O_2Se/BP$ , BP,  $Bi_2O_2Se$  are extracted from the falling edges to be ~ 9 ms,  $\sim 190$  ms, and  $\sim 180$  ms, respectively (Figure 4(d)). The fast response speed of heterojunction is owning to the fast carrier separation at the interface, by which the trapping effect is reduced [14, 26]. However, carriers still suffer from the effects of traps arising from defects in the flakes during the lateral transport. Therefore, the response speed of heterojunction could be further improved by employing higher quality crystals or shortening the lateral channel length. The photoresponse of  $Bi_2O_2Se/BP$  heterojunction to near infrared light (850, 1310 and 1550 nm) are shown in Figures S3 and S4. Interestingly, the device also shows a fast response time (~20 ms) under 1550 nm infrared light (Figure S5). The R and  $D^*$  are extracted and shown in Figure 4(e). Because of the absorption of both BP and  $Bi_2O_2Se$  to infrared light, R reaches ~ 9.5 A/W, ~ 4.3 A/W and ~ 2.3 A/W at 850 nm, 1330 nm and 1550 nm, respectively. This is at a superior level among the BP or  $Bi_2O_2Se$  based photovoltaic photodetectors, as summarized in Figure 4(f) [27–38]. Whilst  $D^*$  is calculated to be ~ 5.3 × 10<sup>9</sup> Jones, ~ 2.4 × 10<sup>9</sup> Jones and ~ 1.3



Figure 4 (Color online) High performance of the Bi<sub>2</sub>O<sub>2</sub>Se/BP vdW heterojunction photodetector. (a) and (b) Power depended R and  $D^*$  of Bi<sub>2</sub>O<sub>2</sub>Se, BP, and Bi<sub>2</sub>O<sub>2</sub>Se/BP heterojunction under 700 nm illumination at  $V_{ds} = -1$  V. (c) Photoswitching response under 700 nm laser illumination at  $V_{ds} = -1$  V. (d) The extracted response time from the falling edge in (c). (e) Power depended R and  $D^*$  of the Bi<sub>2</sub>O<sub>2</sub>Se/BP vdW heterojunction photodetector under three near-infrared waveband light (850 nm, 1310 nm and 1550 nm) at  $V_{ds} = -1$  V. (f) Comparison of the R of Bi<sub>2</sub>O<sub>2</sub>Se/BP vdW heterojunction with other photovoltaic photodetectors based on BP and Bi<sub>2</sub>O<sub>2</sub>Se vdW heterojunction.

 $\times 10^9$  Jones, respectively. The degradation of photoresponse at near infrared can be attributed to the decreasing absorption of BP and Bi<sub>2</sub>O<sub>2</sub>Se at the near infrared band [20,39].

## 3 Conclusion

In summary, a broadband photodetector with high performance has been demonstrated based on  $Bi_2O_2Se/BP$  vdW heterojunction. It possesses responsivity of ~ 500 A/W, ~ 9.5 A/W, ~ 4.3 A/W, and ~ 2.3 A/W at spectral regions of 700 nm, 850 nm, 1310 nm and 1550 nm. Benefiting from the rectification effect and the low dark current of the p-n heterojunction, the detectivity of the device can reach up to ~ 2.8 × 10<sup>11</sup> Jones (700 nm), ~ 5.3 × 10<sup>9</sup> Jones (850 nm), ~ 2.4 × 10<sup>9</sup> Jones (1310 nm) and ~ 1.3 × 10<sup>9</sup> Jones (1550 nm). In addition, the fast separation of carriers at the  $Bi_2O_2Se/BP$  heterojunction enables a faster response time (~ 9 ms), which is more than 20 times faster than individual BP (~ 190 ms) and  $Bi_2O_2Se$  (~180 ms) photodetectors.

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**Supporting information** Figures S1–S5. The supporting information is available online at info.scichina.com and link.springer. com. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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