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Tunneling devices based on graphene/black phosphorus van der Waals heterostructures

Xiao-Qiang Jiang, Xiao-Kuan Li, Shao-Nan Chen, Bao-Wang Su, Kai-Xuan Huang, Zhi-Bo Liu* and Jian-Guo Tian

1 The Key Laboratory of Weak Light Nonlinear Photonics, Ministry of Education, School of Physics and TEDA Institute of Applied Physics, Nankai University, Tianjin 300071, People’s Republic of China
2 The collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi 030006, People’s Republic of China
3 Renewable Energy Conversion and Storage Center, Nankai University, Tianjin 300071, People’s Republic of China
4 Author to whom any correspondence should be addressed.

E-mail: liuzb@nankai.edu.cn

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Abstract

Vertically stacked devices of two-dimensional layered materials (2DLMs) based on van der Waals heterostructures (vdWHs) have recently attracted considerable attention due to their good properties. A tunneling structure is presented in this paper that, unlike other tunneling structures, has no specific insulating two-dimensional materials, such as boron nitride. The tunneling structure is comprised of graphene and black phosphorus. Black phosphorus is chemically active, and can be easily oxidized in the air to form an insulating layer. A tunneling device was produced based on this characteristic of black phosphorus. The insulation layer was an oxide layer formed by the oxidation of black phosphorus. The structure takes advantage of the easy oxidation ability of black phosphorus. The presence of a black phosphorus oxide layer was determined by XPS analysis. The tunneling characteristics of the overlay structure were determined by measuring the current-voltage (I-V) curve of the device. Simulation studies showed that the oxidation layer was responsible for the tunneling effect. Compared with other black phosphorus devices, the photoelectric properties of the proposed device were greatly improved.

1. Introduction

Two-dimensional layered materials (2DLMs), including graphene (Gr), hexagonal boron nitride (h-bn), transition metal dihalides (TMDs), etc., have attracted worldwide attention due to their broad application prospects in next-generation electronic and optoelectronic devices [1–4]. The van der Waals heterogeneous structure (vdWHs) assembled from these materials not only provides the possibility for the preparation of artificial materials with ideal properties, but also provides a platform for the construction of multifunctional devices due to the atomic plane heterogeneous interface and superior performance [4–8]. Typical vdWHs have a barrier-layer sandwiched tunneling structure which exhibits good performance in rectifiers [5, 9], memories [10–12], light-emitting diodes [13], and photodetectors [14]. The surface passivation of this two-dimensional material can be understood by the fact that there are no overhanging chemical bonds on the surface, so van der Waals interactions allow different materials to be superimposed without lattice mismatches. This makes it possible to construct van der Waals heterogeneous structures based on various two-dimensional materials or two-dimensional materials integrated with photon structures [15].

It is also well-established that black phosphorus is unstable compared to other two-dimensional materials. If it is exposed to air for several hours, it will decompose. The surface will form a layer of insulating material POx and thicken over time until it is completely oxidized [16]. Therefore, when the carrier passes through the black phosphorus from the vertical direction, there will be an obvious tunneling phenomenon compared with the horizontal flow. This results in a stronger vertical response than horizontal [17]. Moreover, when the direct band gap of black phosphorus is 0.3 eV, the photoresponsivity is about 4.8 mA W⁻¹ [18].

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There are many two-dimensional materials, such as Bp/MoS$_2$, Bp/Bp, and Bp/Gr, and the applications of such doped materials in the fields of electronics and optoelectronics have been widely studied [17, 19–24]. Most of the methods for enhancing photo-electronics utilize the interaction between two-dimensional materials and photons. Herein, we propose the use of black phosphorus oxidation layer through tunneling effect to improve the photo-electronic properties of two-dimensional materials.

Although bulk black phosphorus is stable for several months under normal temperature and pressure, the thin layer of black phosphorus is unstable under normal conditions, mainly due to water vapor and oxygen in the air [22]. Therefore, when black phosphorus is exposed to the air, it is completely eroded in a few days, while samples comprised of only a few layers are completely oxidized within hours.

In this work, we prepared vertically stacked graphene-black phosphorus-black phosphorus-graphene. We measured the current-voltage ($I_d-V_d$) curve of the sample, which exhibited tunneling characteristics and was symmetrical. However, graphene and black phosphorus are semiconductors without tunneling characteristics. Considering that black phosphorus is easily oxidized in air [22], it can be inferred that the tunneling was caused by POx. At the same time, by comparing Bp, Bp-Bp, Bp-Gr, and Gr-Bp-Gr, it was found that the photoelectric response of the four-layer superimposed structure was larger and reached 0.046 A W$^{-1}$. During the stacking process, the overlap region of black phosphorus was exposed to air for approximately half an hour. Thus, we measured the XPS of the normal black phosphorus sample after exposure to air for the same amount of time.

2. Results and discussion

Figure 1 (a) illustrates the configuration of G-Bp-Bp-G by directional superposition of crystals. The sample was obtained by mechanical stripping and then dry-transferred out of the stripping apparatus. First, a graphene thin film was mechanically exfoliated onto a 300 nm high p-type silicon wafer. Then, the Armchair (AC) direction of the prepared Bp sample was determined by a polarized light microscope on polydimethylsiloxane (PDMS). Two Bp thin layers were stacked on top of a silicon wafer with their AC directions perpendicular to one another. Then, a metal contact electrode (60 nm, Au) was prepared by lithography and magnetron sputtering. Finally, all samples were annealed at 200 °C for 2 h to ensure good contact between Bp, graphene and Au electrodes.

Figure 1 (b) is the optical image of this device with a scale of 2 μm.

Figures 1(c), (d) presents an atomic force microscope (AFM) image of Gr-Bp-Bp-Gr. From the height map, we determined that the upper and lower graphene samples are 4.15 nm and 8.64 nm, and the upper and lower black phosphorus samples are 52.327 nm and 29.30 nm, respectively. Figure 1(e) shows the results of Raman spectroscopy with excitation using a 532 nm laser. Raman spectra were obtained for three different locations of
the sample: a separate graphene sample (red line), a separate black phosphorus sample (black line), and a sample of four overlapping regions (blue line). In the Bp region, the Raman peaks of black phosphorus correspond to $A_{2g}^1$, $B_{6g}^2$, $A_{2g}^2$ at 359, 438, and 464 cm$^{-1}$, respectively. The characteristic peak of the overlap region corresponds to the peak value of each of black phosphorus and graphene.

In the upper panel of figure 1(f), the P 2p spectra is plotted to confirm the formation of POx, where P1, P2, P3 and P4 are shown in red, yellow, purple and blue, respectively. A freshly cleaved Bp crystal was analyzed using x-ray photoemission spectroscopy (XPS) with an Al Kο source. The resulting XPS spectrum of the P 2p$_{3/2}$ core level is shown in figure 1(f), which displays contributions from both Bp and POx. The P 2p$_{3/2}$ peak at a binding energy of 131 eV in P1 and spin–orbit split P 2p$_{1/2}$ peak in P2 are in good agreement with previous observations of Bp XPS spectra. The overlapping P 2p$_{1/2}$ and P 2p$_{3/2}$ peaks at a binding energy of ~134.5 eV in P4 peak are in very good agreement with previous reports for P$_2$O$_5$ [23, 24]. A peak is also observed in the P3 position, which means that the sample contains another phosphorus oxide other than P$_2$O$_5$. It also shows that the types of black phosphorus oxides are not pure.

The sample transfer process is shown in the figure. The sample transfer process uses dry transfer with a transfer medium of PDMS in a ratio of 10:1. The PDMS solidification process involves static cooling at normal temperatures. In addition, PDMS is coagulated into a disposable culture dish. During transfer, the sample is attached to the side closest to the culture dish. Since the surface of the disposable culture dish is uneven, the PDMS is adhered to the black phosphorus or graphene. In the case of silicon wafers, a pressure difference is formed on both sides of the graphene or black phosphorus (air on the side close to the PDMS, not on the side of the silicon wafer), which improves the adhesion of the sample to the silicon wafer. This property is beneficial to the sample transfer.

The electrical properties of Gr-Bp-Bp-Gr were measured at room temperature under ambient atmosphere. Figure 2 shows the $I_d-V_d$ curve of a graphene/ black phosphorus tunnel junction. The sigmoidal shape of the curve is a distinctive feature of electron tunneling through a potential barrier. The reason for tunneling is that black phosphorus tends to form a layer of POx film in the air, and POx is an insulator. Here, we employ the Simmons model for tunneling through symmetric barriers [25]. Figure 2(a) shows a typical curve of a 3-layer sample. Figure 2(b) is an $I_d-V_d$ graph of 4- and 3-layer samples, respectively, of graphene-black phosphorus-graphene. The comparison shows that the tunneling performance of the 4-layer structure is stronger than that of the 3-layer structure, which is due to the increase in the black phosphorus oxide layer. Figures 2(c), (d) show a simulation of the tunneling structure, where the blue lines represent the simulation results and the red dots represent the experimental measurements. The details of the simulation process will be explained below.

It is well known that black phosphorus has anisotropic photoelectronic properties rarely seen in other two-dimensional materials. Carriers (both electrons and holes), following the Armchair (AC) direction of black phosphorus with Zigzag (ZZ) direction mobility are different. For lower quantities of black phosphorus, the AC mobility is only approximate. The AC mobility is 2 to 4 times that in the sawtooth direction. Due to our special stacking method, the carrier is transmitted from top to bottom in the sample, rather than in the two-dimensional plane. We investigated whether black phosphorus still has anisotropy in the vertical direction.

Figure 3 shows the results of our measurement. Figures 3(a)–(d) shows the irradiation of different polarized light spots on the surface of the sample (figure 1(b)) at different power levels of 0.05, 0.5, 1, and 2 mW, respectively.

In this sample, the radial directions of black phosphorus in the middle two layers are perpendicular to each other, and the polarization angle of the spot is transformed based on the radial direction of black phosphorus in the upper layer. That is, 0° polarization indicates that the polarization direction is parallel to the radial direction of black phosphorus in the upper layer.

Although the overall curve characteristics change as the power is increased, the $I_d-V_d$ curves with different polarization angles do not change regularly at the same power, which indicates that black phosphorus does not show anisotropy in the vertical direction in this work.

To further demonstrate the photo-response mechanism, we used a set of self-made scanning photo-current mapping systems to characterize the photocurrent distribution of the entire sample. The final measured results with bias voltages of 1, 0, and −1 V at zero gate voltage are shown in figure 4. In the superposition process, we measured the radial direction using the RGB method, and the stacked black phosphorus samples are perpendicular to each other. By adjusting the polarizer, we measured both the horizontal and vertical polarizations, relative to the upper black phosphorus. The measurement chart is shown in figure 4. Moreover, white arrows in these two pictures represent the direction of linearly polarized light with the horizontal (vertical) arrows parallel (perpendicular) to the channel. The photocurrent scale is indicated by the top color bar. It can be seen from the figure that the image is symmetric when $V_g = \pm 1$ V, and the response is stronger than when $V_g = 0$ V. This is consistent with the measurement of the $I_d-V_d$ curve. By comparing the pictures at the same voltage for vertical and horizontal polarizations, it is evident that the relationship with the polarization direction...
is small, indicating that the radial influence of black phosphorus is small. The figure shows that the photocurrent response is strong where the four layers overlap.

We also evaluated the photo-response performance by calculating the photo-responsivity

$$R_{ph} = \frac{I_{ph}}{PA}$$

where $I_{ph} = I_{\text{photo}} - I_{\text{dark}}$, $I_{\text{photo}}$ and $I_{\text{dark}}$ are the drain currents with and without incident light, respectively, $A$ is the effective area, and $P$ is the light density (assuming that the entire incident light was absorbed). It can be seen from the comparison of the light response ratios of other two-dimensional materials that the light effect rate is higher in the experiment [26]. By comparing Bp, Bp-Bp, Bp-Gr and Gr-Bp-Gr, it was found that the photoelectric response of the four-layer superimposed structure is larger. The reason is that there are more oxidation layers in the four-layer superposition structure, which greatly inhibits the recombination of carriers and enhances the photoelectric response. As seen from table 1, the photoelectric properties of the Gr-Bp heterojunction are distinctly better compared to other black phosphorus devices.

From the photocurrent map, we can determine the area through which the carriers pass, which serves as a prototype for the theoretical simulation. Figure 5(a) shows the oxidation of black phosphorus in the air, that is, $PO_X$ is produced under the combined action of water and oxygen in the air.

The Simmons model [25] is a formula derived from the electrical tunneling effect of an arbitrary-shaped potential barrier existing in an insulating film. This formula applies to rectangular obstacles with and without image power. When the two electrodes are separated by an insulating film, the equilibrium condition requires the top of the insulator’s energy gap to be above the Fermi level of the electrode. Therefore, the role of the insulating film is to introduce a barrier between the electrodes, which hinders the flow of electrons between the electrodes.

Figure 2. Electrical characterization of a graphene/black phosphorus tunneling junction under ambient conditions (a) Schematic diagram of graphene/black phosphorus. The structure has three layers. The top and bottom layers are graphene, the middle layer is black phosphorus. (b) The I–V characteristics of the 4-layer sample and the 3-layer sample at room temperature for graphene-black phosphorus-graphene. (c) Simulation of the 4-layer sample. (d) Simulation of the 3-layer sample. The blue lines represent the simulation results and the red dots represent the experimental measurements.
Current can flow through the insulating region between the two electrodes if:

(a) The electrons in the electrode have enough thermal energy to overcome the potential barrier and flow in the conduction band.

(b) The barrier is thin enough to be penetrated by the electrical tunneling effect. Simmons model can accurately analyze these conditions.

Figure 3. Electrical characterization with different light polarizations of the graphene/black phosphorus tunneling junction under ambient conditions. (a)–(d) show the irradiation of different polarized light spots on the surface of the sample at different power levels of 0.05, 0.5, 1, and 2 mW.

Figure 4. Scanning photocurrent mapping of the graphene/black phosphorus tunneling junction. Pane (a) is an optical microscope image of the heterojunction. Panes (b), (c) and (d) show photoelectric scans of horizontally polarized −1 V, 0 V, 1 V positions. Panes (e), (f) and (g) show an electro-optical scan of the vertical sample −1 V, 0 V, 1 V position. The photoelectron density distribution, that is, the photoelectron passage region, is the sample overlap region.
The current-voltage relationship for a generalized barrier can be described as (Figure 5(b)):

\[ I = J_0 \left\{ \varphi \exp\left(-A\varphi^2\right) - \left(\varphi + eV\right)\exp\left(-A\left(\varphi^2 + eV\right)\right) \right\} \]  

(2)

\[ J_0 = \frac{e}{2\pi h(\beta \Delta s)^2} \]  

(3)

\[ A = \left(\frac{4\pi\beta \Delta s}{h}\right)\left(2m\right)^{1/2} \]  

(4)

\[ \beta = 1 - \frac{1}{2}\int_{s_1}^{s_2} \left\{ f(x) - f^2 \right\} dx \]  

(5)

where \( m \) = mass of electron, \( e \) = charge of electron, \( h \) = Planck’s constant, \( s \) = thickness of insulating film, \( s_1 \), \( s_2 \) = limits of barrier at Fermi level, \( \Delta s = s_1 - s_2 \), \( J \) = tunnel current density, \( V \) = voltage across film, \( V_i \) = image potential, \( \eta \) = Fermi level, \( f(E) = \text{Fermi–Dirac function}, \phi = \text{work function of metal electrode}, \varphi_0 = \text{height of rectangular barrier}, \mu = \text{mean barrier height}, \varepsilon \) = permittivity of insulating film, \( K \) = dielectric constant, and \( \sigma \) = tunnel resistivity (\( \Omega \)-cm\(^2\)).

In this simulation process, we treated the entire sample as an electrode-insulation layer-electrode structure. Then, the rectangular potential barrier in insulating film between metal electrode would be \( V < \varphi_0/e \). We can then simplify the model as (Figure 5(c)):

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**Table 1.** Comparison of the Photovoltaic and Photoresponse Performance Metrics of Our G-Bp-Bp-G van der Waals p-n Junction with Other 2D Heterostructures.

| Stacked          | Responsivity (A/W) | Wavelength (nm) | References |
|------------------|---------------------|-----------------|------------|
| Bp               | \(4.8 \times 10^{-3}\) | 532             | [18]       |
| Bp-MoS\(_2\)     | 2.17                | 582             | [19]       |
| Bp-Bp            | \(4.6 \times 10^{-3}\) | 532             | [17]       |
| Bp-Gr            | \(1.35 \times 10^{-2}\) | 640             | [20]       |
| Gr-Gr-Bp         | \(2.4 \times 10^{-2}\) | 532             | This work  |
| Gr-Bp-Gr-Gr      | \(4.6 \times 10^{-2}\) | 532             | This work  |

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**Figure 5.** (a) Schematic diagram of black phosphorus oxidation. (b) Typical symmetric tunnel junction. (c) Symmetric tunnel junction in this work. (d) Response time spectrum of the sample, with a specific time of 0.07 s.
\[ \Delta s = s \]  
\[ \varphi = \varphi - \frac{eV}{2} \]  

Thus, equation (2) can be transformed into

\[ J = \left( \frac{e}{2\pi \hbar s^2} \right) \left\{ \left( \varphi_0 - \frac{eV}{2} \right) \exp \left[ -\frac{4\pi s}{\hbar} (2m)^{1/2} \left( \varphi_0 - \frac{eV}{2} \right)^{1/2} \right] - \left( \varphi_0 + \frac{eV}{2} \right) \exp \left[ -\frac{4\pi s}{\hbar} (2m)^{1/2} \left( \varphi_0 + \frac{eV}{2} \right)^{1/2} \right] \right\} \]  

From this fit, we obtain a distance of 1.12 nm (±8%) and an effective work function \( \varphi_1 = 2.8 \text{ eV} \) (±10%) for 4-layer sample, and 0.98 nm (±8%), \( \varphi_2 = 2.8 \text{ eV} \) (±10%) for 3-layer sample. The work function is significantly lower than the values obtained by Kelvin probe microscopy on the face of Bp sheets (5.35 to 5.42 eV) and graphene sheets (4.45 to 4.8 eV) [27]. Figure 5(d) shows the response time spectrum of the sample. It can be seen that the specific time is 0.07 s.

3. Methods

A thin graphene flake was mechanically exfoliated onto a 300 nm thick SiO\(_2\)/Si substrate using PDMS. Then, subsequent two-dimensional materials such as black phosphorus were superimposed at one time via dry transfer. Finally, all samples were annealed at 200 °C for 2 h in Ar/H\(_2\) atmosphere to ensure close contact between Bp, graphene, and electrodes. Raman spectroscopy (RENISHAW RM2000, 514 nm) and AFM (Bruker Dimension Icon) were utilized to obtain the heterojunction information. The electronic results and photocurrent were measured by semiconductor parameter analyzer (Keithley 4200A-SCS) under dark and illumination conditions. Scanning photocurrent mapping was performed using the same set of photoelectric measuring devices. A beam of 532 nm laser was passed through mirror, polarizer, quarter-wave plate, vibrating mirror (SUNNY TECHNOLOGY, S-8316D), lens, lens, polarizer, mirror, and objective lens to irradiate the measured samples. Then, the reflected light passed through an objective lens, mirror, and reached the CCD. Through controlling the vibrating mirror with a program, the laser could illuminate different positions to achieve the scanning photocurrent mapping. The current was measured with a high-precision digital source meter (KEITHLEY 2400).

4. Conclusion

In summary, a superposed structure of four layers of samples was fabricated by mechanical peeling. The electrical properties of the samples were measured and their current-voltage (I\(_d\)-V\(_d\)) curves exhibited tunneling effects. By measuring the photocurrent map, it was found that the carrier propagation mode passes from the 4-layer overlapping region instead of sequentially passing through the edge. The tunneling is due to the instability of black phosphorus. Since black phosphorus reacts with water in the air and oxygen, an insulating layer, POx, is formed on the surface of the black phosphorus, which in turn induces a tunneling effect. The light response rate was measured, and found to be 0.046 A W\(^{-1}\) at 1 mW. The oxidizability of black phosphorus is a disadvantage in many cases. The thickness of black phosphorus oxide layer should be controlled to adjust the required photoelectric response.

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ORCID iDs

Zhi-Bo Liu  @ https://orcid.org/0000-0001-9210-156X

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