2D Black Phosphorus/SrTiO₃-Based Programmable Photoconductive Switch

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2D Black Phosphorus/SrTiO₃ based Programmable Photoconductive Switch

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Heterostructures on the nanometer-scale have led to completely new physical behaviors and functionalities. Oxides and two-dimensional (2D) materials are two excellent but isolated platforms for the creation of functional heterostructures. The quasi-freestanding nature of 2D materials allows the realization of heterostructure by stacking different 2D crystals on top of each other in a precise sequence, which is often referred to as van der Waals (vdW) heterostructure^[1-7]. While the ultra-sensitivity of structural distortions and crystal chemistry

from various transition-metal oxide materials^[8] result into a number of novel phenomena at complex oxide interfaces, such as the ferromagnetic metallic states in superlattice composed of antiferromagnetic insulators^[9], the superconductivity and ferromagnetism at interface between two dielectrics^[10, 11], and the enhanced critical temperatures in high- T_c superconductor heterostructures^[12]. The marriage of 2D materials and oxides may provide a scaffold for a large variety of unprecedented heterostructures and novel devices.

Among the transition-metal oxides, one of the most important and widely used constituent materials is strontium titanate (SrTiO_3 , STO). Based on it, a great number of complex oxide structures were built and numerous interesting phenomena have been reported. For example, lanthanum aluminate/strontium titanate ($\text{LaAlO}_3/\text{SrTiO}_3$) interfaces exhibit metallic conductivity^[13], superconductivity and ferromagnetism^[10, 11], which are not found in the constituent materials. Single layer FeSe grown on STO shows superconductivity with T_c above 100 K^[14]. Light induced gating effect or magnetization have also been discovered in the STO or related heterostructures^[15-17].

On the other hand, unusual properties and new phenomena have been revealed in 2D van der Waals solids (vertically heterostructures). Exceptionally high mobility has been observed in the graphene/BN heterostructure^[18]. Light-matter interaction has been greatly enhanced in semiconducting transition metal dichalcogenides (TMDs)/graphene heterostructure, leading to enhanced photon absorption and electron-hole creation^[19]. Light-emitting diodes fabricated by vertically stacked graphene, hexagonal boron nitride and various semiconducting TMD monolayers into carefully designed sequences has exhibited an extrinsic quantum efficiency of nearly 10%^[20]. Ultrafast photoresponse and long lived interlayer exciton have also been observed in the vdW heterostructure^[21-23]. Stacking the functional 2D materials with strongly correlated oxide substrate will open new avenues for heterostructure fabrication, unique properties and novel phenomena are also highly expected, as evidenced by the pioneer work

of high temperature superconductivity in FeSe/STO heterostructure^[14]. Here, we report a new strategy to fabricate heterostructure based on BP, a unique 2D material with high mobility and in-plane anisotropy, and STO, a widely used oxide substrate. In contrast to the BP device fabricated on SiO₂ substrate, remarkable optoelectronic functionalities of the light-tunable persistent photoconductivity with large on/off ratio exceeding 10⁵ was observed in the BP/STO heterostructure.

Similar to graphite and transition metal dichalcogenides (TMDs), black phosphorus (BP) is a layered crystal and has recently been rediscovered from the perspective of 2D material^[24-27]. It has shown excellent electrical properties, including a high hole mobility up to 1,000 cm² V⁻¹s⁻¹^[24], an on/off ratio up to 10⁵, with excellent transport properties^[28-30], has regained remarkable interests for potential applications in high-performance thin-film electronics. Moreover, bulk BP has a bandgap of ~0.3 eV. As the number of layer decreases, the bandgap increases and eventually reaches to 1.8 - 2.0 eV in the monolayer^[31, 32]. Such a layer-dependent bandgap covering the visible to mid-infrared spectral range suggests that BP is a very promising 2D material for broadband optoelectronic applications^[33-35]. Due to the large tunable bandgap, BP has also been used as a broadband absorber from visible to midinfrared range^[36]. With its puckered orthorhombic structure of the D_{2h} point group (**Figure 1a**), the effective mass of carriers of BP along the zigzag direction is about 10 times larger than that along the armchair direction, which induces strong in-plane anisotropy of its electronic, optical, and phonon properties^[25, 37-39]. Such properties may enable a new domain of electronic and photonic device research where the strong anisotropic properties of 2D materials could be used to design new electronic and optoelectronic device applications.

Before investigating the BP/STO heterostructure, we first exfoliate the BP thin flakes on the Si substrate covered with 285 nm SiO₂, and measure the intrinsic field effect mobility and photoresponsivity. A typical optical image and height profile of the BP flake are shown in

Figure 1b. The Raman scattering spectra have used to identify the crystalline orientation of BP flakes as well as the layer number^[40]. Figure 1c shows Raman spectra of BP. We observe three Raman peaks in BP thin flake at around 470, 440 and 365 cm^{-1} , corresponding to the A_g^2 , B_{2g} and A_g^1 modes, respectively, which agree well with previous observations in few-layer BP flakes^[41]. These sharp modes correspond to the unique orthorhombic crystalline phosphorus structure (Fig. S2). In addition, TEM characterization (See Fig. S1) also confirms the highly crystalline structure of BP.

BP field-effect transistor is fabricated through photolithography on Si/SiO₂ substrate. We perform electrical characterizations of our devices in a vacuum chamber at room temperature, the transfer and output curves are shown in Figure 1d and e, respectively. The nearly linear I_d - V_d curve at low voltage indicates the low Schottky barrier at the metal/BP interface. The transfer curve reveals a p-type behavior of the BP devices. By fitting the I_d - V_g curve in the V_g from -10 V to -30 V, the mobility of the channel is deduced to be 149 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, calculated by using the equation $\mu = dI_d/dV_g \times (L/WC_iV_d)$, where L is channel length (4.5 μm), W is the channel width (9 μm) and C_i is the capacitance between the channel and the back gate per unit area ($C_i = \epsilon_0 \epsilon_r/d$; ϵ_0 is vacuum permittivity, ϵ_r is the relative permittivity, and d is the thickness of SiO₂ layer of 285 nm). The calculated mobility is comparable with other reported value^[24, 27]. Due to the semiconducting nature of BP, the transistor shows an on/off ratio of around 10^5 . We then evaluate the photoresponse of the fabricated BP FETs. The measurements are carried out by mechanically modulating the intensity of the incoming light (633 nm) and recording the current under constant $V_d = 5$ V and -40 V gate bias. Figure 1f shows the measured photocurrent with light power of 2 mW, which is in phase with the excitation modulation. The photoresponsivity R , calculated by $R = I_{ph}/P$ (I_{ph} is generated photocurrent, P is the light power absorbed by the device channel), is around 2.5 A/W, higher than the reported value of 0.66 A/W^[34]. This might be due to the difference of the applied gate

voltage and drain voltage, which can tune the Schottky barrier height and electron-hole separation rate for the photocurrent generation, respectively.

In contrast to the SiO₂ substrate, STO dramatically change the behavior of the device due to strong interaction between the layers. Details of the device fabrication are shown in the method part (Fig. S3). The photoresponse properties of the heterostructure device were carried out at low temperature (50 K). As can be seen in **Figure 2a**, the current increases step by step with switching on and off the red light illumination, which is in contrast with the photoresponse behavior of BP device on SiO₂. Even though a high photocurrent is obtained, 2s illumination of UV light makes current drop dramatically. Figure 2b shows the time dependent photocurrent of the device with a few cycles of alternative red and UV light illumination. The photocurrent periodically increases and decreases upon the light-on and light-off conditions at a 1 V bias voltage, respectively, indicating excellent response and reliability of the device. Figure 2c shows the I_d - V_d curves under ON and OFF states at 50 K. The current on/off ratio of the device were achieved to $\sim 10^5$, significantly higher than that of the reported photodetection device based on other 2D materials like graphene^[42], TMDs^[43] and a few order of magnitudes higher than pristine BP^[35], which is also larger than the hybrid device based on graphene/MoS₂^[44]. By subtracting the OFF current from the ON current, the responsivity of light induced current change is calculated to be 1.1×10^5 A/W, which is about 10^5 times larger than that of the photoresponse for the BP phototransistor integrated with waveguide^[34], and comparable with the recent reported value based on BP device with narrow channel length (but with very low on/off ratio)^[45]. In addition to the high photosensitivity of the heterostructure device, the current can keep a long time. As shown in Figure 2d, the current almost keeps constant for more than 4 hours. A decay time of several days can be deduced by fitting the experimental data. We also compared the room temperature photoresponse of BP/STO heterostructure with BP device on SiO₂ substrate. Significant

different behavior is also observed even at room temperature (see Fig. S4). Similar persistent photocurrent behavior is also observed in MoS₂/STO heterostructure (Fig. S6).

To understand the tremendously enhanced responsivity (~ 5 orders) as well as persistent photocurrent in the heterostructure device, we perform the wavelength dependent photoresponse measurement. As can be seen in **Figure 3a-c**, under the fixed illumination light intensity, the photocurrents induced by the illumination of 633 nm, 532 nm and 405 nm are $\sim 1.8 \mu\text{A}$, 120 nA and 25 nA, respectively, indicating that wavelength plays an important role in the enhancement of responsivity and persistent photoconductivity. This phenomena can be explained by a model based on electron-hole generation and recombination process related to optical absorption and defects in STO^[17]. Generally, there are numerous donor and acceptor states generated by intrinsic defects in STO^[46, 47]. Due to the variation in absorption, the optical penetration depth and excited energy state of different state changes accordingly depending on the wavelength of the incident light. For example, UV light can excite both the deep and low defect levels but within very limited thickness below the surface (Fig. 3e). While red light could penetrate through the entire sample, and excite the low defect levels (See absorption spectrum of STO in Fig. S5). Under light illumination, the semiconductor heterostructure undergoes various electron-hole pairs generation, diffusion, and recombination process. The UV light only generates electron-hole pairs close the surface layer. If the generated electrons diffused to the deep inside layer and recombines with the acceptor centers there, they will be unlikely to be re-excited and remains there even after the light is switched off (Fig. 3e). This results in a built-in electric field at the interface of BP and STO, due to the accumulation of holes at the surface of BP. As a consequence, electrons are accumulated in the BP layer, reducing the photoconductivity of BP due to its p-type nature. In contrast, red light can excite the frozen electrons from the acceptor states located in the deep layer, which recombines with holes at top layer (Fig. 3f). Meanwhile, the built-in electric field

is cancelled, and photoconductivity of BP layer increases. This light-tunable effect at the BP/STO interface enables a high responsivity and persistent photoconductivity in black phosphorus.

To further explore the optical gating induced persistent photocurrent, we examine the temperature dependence of photoresponse from room temperature down to 50 K. The time dependent response of the three processes are studied: (I) the current rising process under the illumination of red light, (II) the current decaying process just after the red light is off (ON state), (III) the current decay process after the UV light is off (OFF state). The normalized time resolved current change of each process are shown in the Fig. S7-S9. The time constant at various temperatures are obtained via fitting and they are plotted in **Figure 4**. When shed the red light on device, the relaxation time is mainly determined by the trap level. Therefore,

we fit experimental data (sphere symbol) by using $\frac{e^{T_0/T}}{T}$, and both are in excellent agreement.

When red light is off, the relaxation process can be attributed to scattering, which gives $\tau \propto T^{3/2}$. Using this scaling to fit red decay time (red solid sphere) gives a good agreement. For UV decay time, we use a combination of exponential function and power law to account for the combined effects from defects scattering and trap excitation.

In conclusion, we have observed the giant photoresponsivity in BP/STO heterostructure. The responsivity of light induced current change exceeds 10^5 A/W. Also, persistent photocurrent effect is observed at low temperature, where the photocurrent is not relaxed after the light is switched off. The on/off ratio achieves 10^5 . The experimental results can be accounted by the optical gating effect at the interface of BP/STO, which is consistent with the theoretical model based on the charge transfer under light illumination. This work opens the door to new type of heterostructures consisting of 2D material and oxides, and will pave a way to novel optoelectronic and memory devices.

Experimental Section

Characterization of BP thin flakes transistor: First the BP flakes were obtained by means of mechanically exfoliation of bulk single crystal on the Si or SrTiO₃ substrates, and identified by optical microscopy. The electrodes (Cr/Au (5/50 nm)) are then patterned with standard photolithography, electron beam metal deposition and lift-off. Atomic Force Microscopy (AFM) is used to determine the thickness of BP flake under the AC mode.

Raman characterization: Raman measurements are performed in a Witec system in backscattering configuration. The excitation is provided by visible laser light ($\lambda = 532$ nm) through a 100 $\times$ objective (NA = 0.95). To avoid laser-induced modification or ablation of the samples, all spectra were recorded at low power levels. For the polarization resolved Raman measurement, the angle between excitation light and the crystal *b*-axis is tuned by rotating the crystal while keeping the excitation light unchanged.

Optoelectronic measurement: All the electronic and optoelectronic characterization are performed in a probe station under vacuum condition, where the temperature can be tuned from room temperature to 50 K. The photocurrent was recorded by the Agilent 1500A semiconductor analyzer under global illumination condition. The light excitation is provided by diode pumped solid state lasers operated in continuous wave mode with different wavelengths of 405 nm, 532 nm, and 633 nm, respectively. The 365 nm lamp was used for the UV excitation.

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Figure 1. Characterization of the BP FET device and photoresponse on SiO₂ substrate. a) Crystal structure of BP. b) Typical optical image (top) and height profile (bottom) of the BP thin flake on SiO₂ substrate. Scale bar, 10 μm . c) Raman spectrum of BP thin flake. d,e) The typical output (d) and transfer (e) curve of BP FET on SiO₂ substrate. Inset of (d) shows the schematic of BP/SiO₂ heterostructure. f) Time dependent photocurrent change of BP transistor on SiO₂ substrate measured at room temperature, with a gate voltage of -40 V and drain voltage of 5 V.

Figure 2. Photoresposne and persistent photocurrent of BP/STO device at 50K. a) The photocurrent change with only red light is switched on and off alternately at 50 K. Red light induced a persistent photocurrent and it does not saturate after a few times illumination. The current remains even the light is off. UV light will reset the current close to zero in a short time (~ 2 s). b) The photocurrent change with both red and UV is switched on and off alternately at 50 K. c) The I_d - V_d curve of the device under the on and off state indicated in (b). Inset shows the polt in semi-log scale. d) Nearly relaxation-free nature of persistent photocurrent at on and off states, respectively. Inset shows the schematic of BP/SrTiO₃ heterostructure.

Figure 3. Light wavelength dependent photoresponse of BP/STO device. The photocurrent evaluation under the illumination of red (a), green (b) and blue (c) light illumination at 50 K. d), Schematic of the BP/STO heterostructure. e,f) The photocarriers generation, transport and recombination dynamics under UV (e) and red (f) light illumination, respectively.

Figure 4. Time constants as a function of temperature for different processes. The time constant was obtained by fitting the current change at the initial stage just after the red (UV) light is switched on/off. The black, red and blue spheres represent the time constant of the current rising process just after the red light is on (black), the current decay process just after the red light is off, the current decay process just after the UV light is off. The solid lines are the fitting results using different function.

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A novel heterostructure is designed by stacking 2D black phosphorus (BP) on SrTiO₃ substrate. The device demonstrate programmable photoconductive switch under illumination of UV and red light. The light-tunable persistent photoconductivity exhibits large on/off ratio exceeding 10^5 . The persistent state shows almost no relaxation or decay at low temperature. These effects could lead to new generation optoelectronic devices for memory application.

Keywords: 2D materials, Black phosphorus, heterostructure, photoconductivity, SrTiO₃

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Title: **2D Black Phosphorus/SrTiO₃ based Programmable Photoconductive Switch**

ToC figure

Supporting Information for

2D Black Phosphorus/SrTiO₃ based Programmable Photoconductive Switch

Fucai Liu, Chao Zhu, Lu You, Shijun Liang, Shoujun Zheng, Jiadong Zhou, Qundong Fu, Yongmin He, Qingsheng Zeng, Hong Jin Fan, L. K. Ang, Junling Wang, Zheng Liu.*

The file includes:

1. TEM characterization of BP flake
2. Angle resolved Raman spectrum of BP flake
3. Room temperature photoresponse of BP/STO heterostructure device
4. Transmission spectrum of STO single crystal
5. Photocurrent change of MoS₂/STO heterostructure
6. Time-resolved photocurrent change at different temperatures.
7. Effect of temperature on relaxation time

1. TEM characterization of BP flake

For TEM observations, BP flakes were directly transferred onto an amorphous holey silicon nitride (SiN) TEM grids (Norcada, Inc.), and then the suspended regions on the selected BP samples were characterized using an FEI Tecnai G2-F20 TEM which was operated at an accelerating voltage of 200 kV; the electron dose was reduced to minimize the radiation damage. As illustrated in Figure S1, high-resolution TEM (HRTEM) were carried out to identify the crystalline orientation; The measured lattice spacings are 0.341 nm and 0.452 nm in the (100) direction and in the horizontal direction for the (001) lattice, respectively. These results match well with the lattice orientation along zigzag and armchair directions, respectively.

2. Angle resolved Raman spectrum of BP flake

Raman spectrum has been used to reveal the crystal orientation of BP flakes. In the angle resolved Raman measurement, an analyzer was placed before the spectrometer to allow for the analysis of the scattered light polarized parallel and perpendicular to the incident light polarization (parallel and cross-polarization configurations, respectively). The angular dependence of Raman response was obtained by rotating the sample. Figure S2 (a) shows the typical Raman spectrum of BP thin flakes at different angles under the parallel configurations, which shows strong angle dependence. To identify the crystal orientation, the intensity of A_g^2 peak is plotted as a function of the polarization angle (Figure S2b).

3. Room temperature photoresponse of BP/STO heterostructure device

Red (633 nm) and UV (365 nm) light source are employed to characterize the photoresponse in both BP and STO layer of the heterostructure device at room temperature, we use red (633 nm) and UV (365 nm) light as the illumination sources. Interestingly, with alternative red and UV light illumination, the drain current of BP is dramatically changed. As shown in Figure

S4a, when we shed red light on the device, the drain current increases quickly, and keeps almost constant even turning off the red light. Surprisingly, such drain current will drops quickly upon UV light illumination. Under the dark state with UV light off, the current increases slowly. These cycles of change in current can be reproduced very well. Figure S4b shows the I_d - V_d characteristics of the device under ON (after red light illumination) and OFF (after UV light illumination) state, respectively.

4. Transmission spectrum of STO single crystal

The transmission spectrum of a STO single crystal with a thickness of around 500 μm is shown in Figure S5. We can see that more than 50% light can go through the single crystal at wavelength of 633 nm, while at short wavelength of 365 nm, almost no light transmitted through the crystal.

5. Photocurrent change of MoS₂/STO heterostructure

We also fabricated the heterostructure based on MoS₂ and STO. The photoresponse of MoS₂/STO heterostructure is shown in Figure S6. Interestingly, the device also shows large photoresponse and persistent photocurrent. But different from the BP/STO device, the photocurrent of the MoS₂/STO heterostructure first increase under the UV irradiation for short time, and then keep almost constant after the UV light is switched off. When the red light illumination in on, the photocurrent decreases gradually. The current shows a suddenly drop just after the red light is switched off, and then becomes constant. This is due to that n-type nature of MoS₂, opposite to the p-type nature of BP, resulting in the reversed photoresponse of MoS₂ and BP heterostructure device.

6. Time-resolved photocurrent change at different temperatures.

To further understand the optical gating effect induced persistent photocurrent, we studied the time resolved photoresponse from room temperature down to 50 K. The time dependent response of the three processes are normalized and studied in details, which are (I) the current rising process under the illumination of red light, (II) the current decaying process just after the red light is Off (ON state), (III) the current decay process after the UV light is off (OFF state). The results are shown in Figure S7–S9, respectively. The traces of red decay curve at 50K shows different behavior which may due to the fast frozen of the electrons at low temperature, and we did not discuss it in Figure 4 in the main text. Other traces can be fitted very well by a simple exponential function and the time constants for each process can be deduced, which are discussed in the main text.

7. Effect of temperature on relaxation time

In the semiconductor, the important scattering mechanisms for electrons are usually due to phonon scattering and defect/impurity scattering. In the SrTiO₃ (STO), there are some electron traps, which can be attributed to oxygen vacancy or iron transition-metal /oxygen vacancy defects. Generally, the oxygen vacancies are the most common in perovskites. The presence of these defects or vacancy creates a series of deep-level or shallower traps in STO. Without defects or impurity, the electron relaxation time τ can be solely determined by the phonon time τ_0 at different temperatures. However, τ will be affected due to the presence of traps induced by defects in the STO, namely $\tau_t = \tau_0 e^{\frac{E_0}{k_B T}}$. Here E_0 is the activation energy of traps and k_B is the Boltzmann constant. When the electrons are trapped, the relaxation time can be reduced as temperature increases. In other word, when increasing the temperature, electrons trapped gain higher energy and it is more likely to be released from traps. Thus it is much faster to reach equilibrium. But for given temperature, the higher activation barrier of trap can keep electrons trapped for very long time as shown in the main text. In the presence of impurity, the scattering between electrons and impurities can influence the relaxation time.

Usually the relaxation time is mainly determined by the electron energy, which is given as

$\tau_i = E^{\frac{3}{2}}$. With the variation in temperature, the τ is considered to be approximately

proportional to $T^{\frac{3}{2}}$. If both of two types of scattering mechanisms come into play, then

Matthiessen's rule must be used to account for the overall effect of temperature on relaxation

time. Then $\tau^{-1} = \sum_j \tau_j^{-1}$, j represents different scattering mechanism.

Figure S1. HRTEM image of the typical BP flake. Inset shows the corresponding FFT pattern.

Figure S2. Angle dependent Raman characterization of BP thin flakes. a) A typical Raman spectrum of BP thin flakes at different detection angles. b) The A_g² peak intensity plotted as a function of the polarization angle. The red line is the fitting results using the sinusoidal function.

Figure S3. Typical optical image of the BP/STO device.

Figure S4. Photoresponse of the BP/STO device at room temperature. a) Photocurrent change as a function of time with the red and UV light switched on and off alternately. The top panel shows the light on and off states as a function of time. b) I_d - V_d curve under the on and off state, respectively. Inset shows the schematic of BP/SrTiO₃ heterostructure.

Figure S5. Typical transmission spectrum of 500 μm thick STO single crystal. The position of 365 nm and 633 nm are indicated by the arrows.

Figure S6. The current change of MoS₂/STO heterostructure as a function of time under different light illumination states. The state of the UV and red light on and off is indicated by arrows in the figure.

Figure S7. The time dependent change of the photocurrent just after red light illumination is on. The solid lines are fitting to the experimental results.

Figure S8. The time dependent change of the photocurrent just after red light illumination is off. The solid lines are fitting to the experimental results.

Figure S9. The time dependent change of the photocurrent just after UV light illumination is off. The solid lines are fitting to the experimental results.