Wavelength-Controlled Photocurrent Polarity Switching in BP-MoS₂ Heterostructure

Himani Jawa,[†] Sayantan Ghosh,[†] Abin Varghese,^{†,‡} Srilagna Sahoo,[†] and Saurabh Lodha^{*,†}

†Department of Electrical Engineering, IIT Bombay, Mumbai, Maharashtra 400076 ‡Department of Materials Science and Engineering, Monash University, Clayton, Victoria, Australia 3800

E-mail: slodha@ee.iitb.ac.in

Abstract

Layered two-dimensional van der Waals (vdW) semiconductors and their heterostructures have been shown to exhibit positive photoconductance (PPC) in many studies. A few recent reports have demonstrated negative photoconductance (NPC) as well that can enable broadband photodetection besides multi-level optoelectronic logic and memory. Controllable and reversible switching between PPC and NPC is a key requirement for these applications. This report demonstrates visible-to-near infrared wavelength-driven NPC and PPC, along with reversible switching between the two, in an air stable, high mobility, broadband black phosphorus (BP) field effect transistor (FET) covered with a few layer MoS₂ flake. The crossover switching wavelength can be tuned by varying the MoS₂ bandgap through its flake thickness and the NPC and PPC photoresponsivities can be modulated using electrostatic gating as well as laser power. Recombination-driven NPC and PPC allows for reversible switching at reasonable time scales of a few seconds. Further, gate voltage-dependent negative persistent photoconductance enables synaptic behavior that is well-suited for optosynaptic applications.

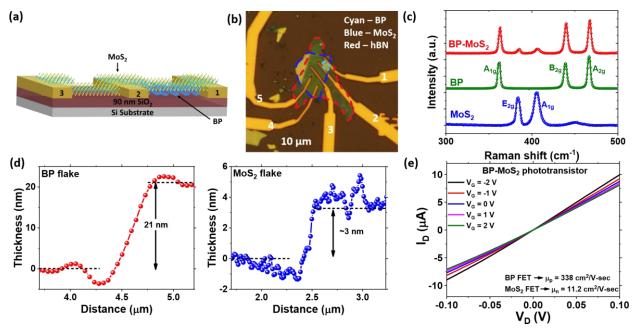
Introduction

Heterostructures based on layered van der Waals (vdW) materials have recently gained significant interest owing to the realization of a variety of optical^{1–8} and electrical^{9,10} phenomena. Stacking different 2D materials offers various advantages such as a wide optical detection range, enhanced photoresponse due to ease of carrier separation, clean interfaces due to the absence of dangling bonds and defects resulting from lattice mismatch. This makes them an excellent choice for photodetection applications. Generally, the device architecture and choice of 2D materials in these heterostructures have been shown to enhance the positive photoconductance^{1,11–14} (PPC) for application areas such as photodetectors¹⁵ or optical memories.^{16,17} However, some recent studies have also shown the possibility of realizing negative photoconductance^{18–23} (NPC) in 2D material-based devices.

The observation of negative photoconductance along with PPC in photodetectors can enable broadband photoresponse with enhanced spectral resolution²⁴ due to their ability to segregate different wavelengths with distinct conductance states. Furthermore, the availability of additional states (PPC and NPC) expands the application scope of 2D materials to multi-bit logic and memory devices. However, the ability to switch reversibly and controllably between NPC and PPC is a critical and unexplored requirement for the realization of logic, memory and optical communication technologies.¹⁸ In addition, NPC, as observed in 2D materials-based devices,^{25,26} could be related to trap centers,²⁷ interaction with adsorbates,²⁸ the bolometric effect²⁹ or dependent on gate bias.²⁰ The first three mechanisms increase carrier scattering in the device resulting in mobility degradation and negative photocurrent. Interface/adsorbate/bulk trap-related mechanisms are difficult to control since it is not trivial to engineer trap densities, distributions and time constants, whereas gate voltage-dependent NPC and PPC adds to the overall power consumption. Recently NPC has been reported in a WS₂/rGO hybrid structure under infrared light as a result of recombination between photogenerated electrons in WS₂ with holes in rGO.¹⁹ NPC has also been reported in an ReS₂/hBN/MoS₂ heterostructure floating gate device with excellent memory properties.¹⁸ These recent reports suggest new avenues for realizing NPC and controlled NPC-PPC switching based on heterostructures using 2D materials.

In this work, we demonstrate wavelength-driven (visible-to-near infrared) NPC and PPC, along with reversible switching between the two, in an air-stable BP FET covered with a few layer MoS₂ flake. BP is chosen for its high hole mobility and broad spectral response (visible as well as NIR) and MoS₂ is chosen for its air-stability, optical bandgap tunability and spectral response in the visible range. The NPC is a consequence of light absorption in the MoS₂ flake, which results in photocarrier generation. Photogenerated holes are captured by intrinsic traps in MoS₂ whereas the photogenerated electrons diffuse towards the BP/MoS₂ heterointerface to recombine with holes in the BP channel leading to a reduction in the net device current under illumination. As the wavelength is increased beyond the absorption edge of the MoS₂ flake, the phototransistor exhibits PPC solely based on the positive photoresponse of the BP flake. The critical wavelength for the crossover between NPC and PPC can be tuned through an appropriate choice of the MoS₂ flake thickness that determines its bandgap and absorption edge. The wavelength-driven NPC-PPC switching is reversible over multiple wavelength cycles, with rise and fall times of a few seconds, and the negative and positive photoresponsivities in the visible and NIR regimes can be tuned using electrostatic gating or laser power. Hence, a broad and tunable spectral response with distinct NPC and PPC regimes, that can be reversibly switched between using wavelength cycling, has been realized in a BP/MoS₂ heterostructure phototransistor. The presence of gate voltage-dependent negative persistent photoconductance makes this device promising for optosynaptic applications as well.

Results and discussion



Device Fabrication and Electrical Characterisation

Figure 1: **Device schematic, fabrication and characterization.** (a) Schematic of BP/MoS₂ phototransistor (b) Optical microscope image showing BP/MoS₂ phototransistor with source/drain metal contacts sandwiched between BP and MoS₂ layers. hBN flake on the top precludes any ambient effects. (c) Raman spectra acquired for the BP/MoS₂ phototransistor (d) AFM scan for BP and MoS₂ flakes (e) Output characteristics of the phototransistor showing ohmic contacts and low gate modulation.

BP flakes were mechanically exfoliated on a 90 nm SiO₂/Si substrate using scotch tape. Source/drain contacts were then formed on the few layer BP flake using electron beam lithography (EBL) and metal deposition (Cr/Au ~ 5/40 nm). An additional contact was fabricated adjacent to the source/drain contacts of the BP FET. Next, MoS₂ flakes were mechanically exfoliated onto a polydimethylsiloxane (PDMS) stamp and large, thin flakes were transferred on to the FET to ensure complete coverage of the BP flake and the extra contact. Further, contacts were formed on the MoS₂ flake using EBL and metal deposition (Cr/Au ~ 5/40 nm). Table S1 shows a set of 10 such devices with their respective BP and MoS₂ flake thicknesses. Figure 1a shows a schematic of the BP/MoS₂ phototransistor (device 1). An optical microscope image of the fabricated device is shown in Figure 1b with the phototransistor covered with an hBN flake (~ 10 nm) to preclude any trapping effects from adsorbates on the electrical and optical characterisation of the phototransistor. The contacts, labelled in the figure are as follows: contacts 1 and 2 sandwiched between BP and MoS₂ flakes for BP/MoS₂ phototransistor, contacts 2 and 3 being formed below the MoS₂ flake in order to quantitatively segregate its contribution in the phototransistor, and contacts 4 and 5 formed on top of the MoS₂ flake to understand its individual optical behavior. To check the crystallinity of the flakes after fabrication, Raman scans for individual materials as well as the overlap region were done. As shown in Figure 1c, Raman peaks at 384 and 405.56 cm⁻¹ correspond to E_{2g} (in-plane vibration) and A_{1g} (out-of-plane vibration) modes for MoS₂ whereas peaks at 363.1, 439.7 and 467.5 cm⁻¹ indicate the A_{1g} , B_{2g} and A_{2g} peaks for the BP flake. The characteristic peaks for both materials being distinctly present in the overlap region confirms the crystalline nature of the exfoliated flakes. Further, thickness of BP and MoS₂ flakes obtained using atomic force microscopy (AFM) are shown in Figure 1d.

Individual field effect transistor performances were studied for the BP and MoS₂ FETs. Their transfer and output characteristics are shown in Figure S1 of the Supporting Information. The BP FET, with a hole mobility of 338 cm²/V-sec (calculated at maximum transconductance) shows slight gate modulation in transfer characteristics (I_D-V_G), shown in Figure S1a, with a high positive threshold voltage (> 5 V). On the other hand, the MoS₂ FET, measured between contacts 4 and 5, shows good gate tunability of I_D (shown in Figure S1c) with an electron mobility of ~11 cm²/V-sec. The output characteristics of the MoS₂ FET with contacts below (contacts 2 and 3) and above the flake (contacts 4 and 5) highlight their ohmic behavior with the currents being slightly higher for contacts 4 and 5 made above the flake, as shown in Figure S1b and S1d. The output (I_D-V_D) characteristics of the phototransistor, as shown in Figure 1e, indicate a major contribution to the current from the BP flake (~ μ As) as compared to a few nAs from the MoS₂ flake with low gate modulation.

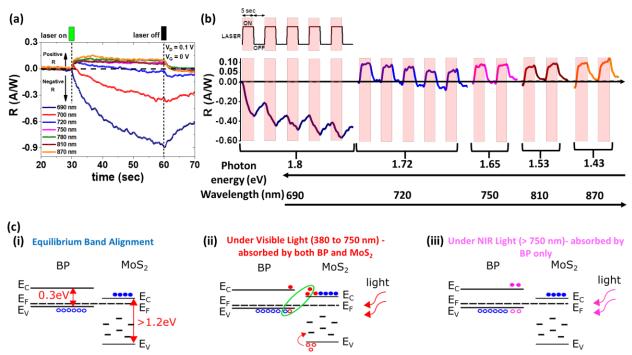


Figure 2: **Wavelength-dependent photoconductance and related band diagrams.** (a) Responsivity versus time for the BP/MoS₂ phototransistor showing negative responsivity for λ < 750 nm and positive responsivity for λ > 750 nm at V_G = 0 V and V_D = 0.1 V (b) Photoswitching with on and off time being 5 sec at V_G = 0 V and V_D = 0.1 V for different wavelengths. (c) BP-MoS₂ energy band alignment at V_G = 0 V for (i) equilibrium conditions, (ii) under visible light, where both BP and MoS₂ absorb light resulting in interlayer recombination and hence, negative photocurrent, and (iii) for NIR illumination, which is absorbed only by the BP flake and hence, positive photocurrent is observed.

Optoelectronic Characterisation of the BP/MoS₂ Phototransistor

Photoresponse of the BP/MoS₂ heterostructure was obtained under 690-900 nm laser illumination. The light was incident on the phototransistor for 30 seconds and then turned off. The photoresponsivity (R) was calculated using the equation: $R = I_{ph}/P_{in}$, where $I_{ph} = I_{light}$ - I_{dark} with I_{light} and I_{dark} being the currents with and without illumination and P_{in} is the incident optical power. As shown in Figure 2a, responsivity is negative for wavelengths (λ) upto 720 nm and positive beyond 750 nm for gate (V_G) and drain (V_D) voltages of 0 and 0.1 V respectively. The negative R can be explained from the band alignment of the BP and MoS₂ flakes in the transverse direction (along gate-SiO₂-BP-MoS₂). Under equilibrium, BP/MoS₂ forms a type-II heterostructure with a band alignment as shown in Figure 2c(i). Both BP and

MoS₂ absorb visible light (λ < 750 nm) illuminated on the overlap region, with MoS₂ absorbing more than BP, thereby leading to generation of electron-hole pairs. The photogenerated holes in MoS₂ get captured by the shallow intrinsic traps distributed near its valence band³⁰ giving rise to excess electron concentration. These excess electrons diffuse towards BP due to the concentration gradient set up by a lower concentration in BP, leading to interlayer recombination with the high hole concentration of BP (Fig. 2c(ii)). This results in a reduction in free hole concentration in BP giving rise to a negative photocurrent or responsivity (as seen in Figure 2a), since BP is the main photoconducting layer in this BP-MoS₂ stack. As the wavelength is increased beyond 750 nm, a positive I_{ph} is observed which can be attributed to (i) negligible optical response from the thin MoS₂ flake limited by its bandgap and (ii) photogenerated carriers in the smaller bandgap (0.3 eV) BP flake. The optical response of the MoS₂ FET (contacts 4 and 5) to 690 and 720 nm incident light is shown in Figure S2a of Supporting Information. MoS₂ does not respond to illumination beyond 720 nm due to its bandgap and therefore, the crossover wavelength λ_t , defined as the wavelength at which the I_{ph} transitions from negative to positive values, is limited by the bandgap of MoS₂. Figure 2b and S3a of Supporting Information show the transition from negative to positive responsivity and photocurrent when the phototransistor was illuminated under different wavelengths with the laser being switched on and off every 5 seconds for each λ .

Gate Voltage and Laser Power Dependent Photocurrent Modulation: The interlayer recombination occurring at the BP/MoS₂ interface under visible light, as discussed above, depends on (i) the electron concentration of MoS₂ (n_M) and (ii) hole concentration of BP (p_{BP}). These carrier concentrations are modulated by the applied gate bias electrostatically and optically and light intensity respectively. Also, the hole concentration in BP is affected by the trapping and detrapping at the BP/SiO₂ interface which varies with applied gate bias.³¹ This results in a dual effect of V_G on the carrier concentrations and hence,

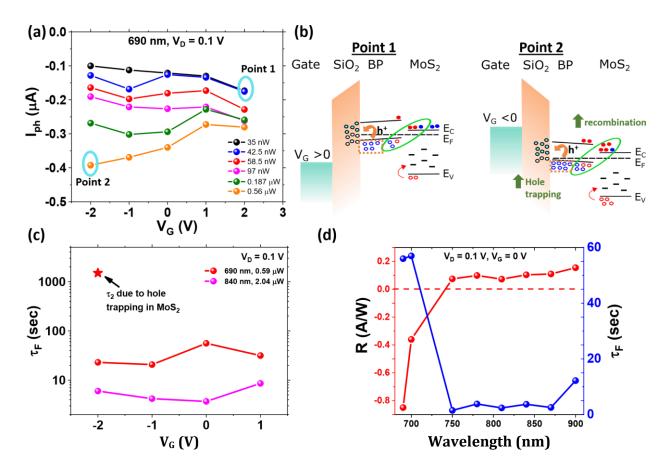


Figure 3: **Gate voltage, laser power and wavelength dependence of temporal response and photocurrent.** (a) Variation of photocurrent as a function of gate voltage under 690 nm illumination (b) Energy band diagrams at points 1 and 2 of figure (a) (c) Fall time (τ_F) vs V_G for 690 and 840 nm illumination indicates faster operation under NIR (d) Responsivity (R) and τ_F as a function of wavelength. Negative responsivity and higher fall times correspond to the optical sensing of MoS₂ in the phototransistor.

on the interlayer carrier recombination. Under illumination for varying V_G, the I_{ph} (dependent on carrier recombination) will be maximum where the effective electron and holes concentrations in MoS₂ and BP respectively will be nearly equal (as shown in Figure S4). The I_{ph} will gradually reduce with V_G on both sides of the maximum point due to reduction in either holes or electrons at positive and negative V_G respectively, since the recombination is limited by the minority carrier concentration. This results in a U-shaped photocurrent plot (I_{ph} vs V_G at P_{in1} in Figure S4b).

Figure 3a shows the variation in photocurrent with gate voltage for varying incident power of 690 nm illumination. The photocurrent magnitude shows a slight increase with increasing gate voltage at low laser powers, a U-shaped variation at intermediate powers (e.g. at 0.187 μ W, similar to the theoretical expectation illustrated in Figure S4b) and a more pronounced change (decrease) in its value at higher optical powers. At lower optical power, most of the electron-hole pair generation takes place in MoS₂. Given the trapping of photogenerated holes in MoS_2 and a high hole concentration in BP, the interlayer recombination is limited by the MoS₂ electron concentration ($n_M < p_{BP}$). The electron concentration in MoS₂ increases with increase in gate voltage (as the device transitions from subthreshold to ON state, as shown in Figure S1c of Supporting Information). Hence, a slightly higher interlayer recombination at positive V_G leads to slightly higher I_{ph} as shown by the band diagram for point 1 in Figure 3b. At lower optical powers, we observe only the left (increasing) I_{ph} branch of the U-shaped curve at P_{in1} in Figure S4b. As the optical intensity is increased, n_M increases due to an increase in the photogenerated carriers in MoS₂. This leads to interlayer recombination being limited by p_{BP} , which gets affected by the trapping and detrapping of holes at the BP/SiO₂ interface.³¹ As V_G is reduced from positive to negative values, the traps at the BP/SiO₂ interface above the Fermi level (E_F) of BP get filled with holes, going from neutral to positively charged. This results in the reduction of free hole carrier concentration in BP as well as of the effective negative gate bias, similar to the left-shift in the U-shaped curve at higher optical power Pin2 of Figure S4b. In order to compensate for this reduction in hole concentration, a more negative V_{G} is required and hence, maximum photocurrent is shifted towards negative V_G, as shown at point 2 in Figure 3b. In the case of higher optical powers, we observe only the right (decreasing) branch of the U-shaped Iph curve at P_{in2} in Figure S4b.

When the phototransistor is illuminated with 780 nm laser (NIR), a positive photocurrent is observed, as shown in Figures S3b and S3c of Supporting Information for varying optical power and gate voltage respectively. This positive I_{ph} increases as the input incident power increases due to an increase in the photogenerated carrier concentrations in the BP flake, as shown in Figure S3b of Supporting Information. The photocurrent also increases as the gate

voltage is increased from negative to positive values. This can be explained by increased concentration of photogenerated free carriers at positive V_G as compared to negative V_G with the maximum photocurrent occurring at maximum transconductance value.³² This is due to dominant photogating effect at the maximum transconductance operating point. Since the BP FET is in the accumulation region for the given V_G range, the I_{ph} increases with increase in V_G .

Temporal Photoresponse: Next, temporal measurements were carried out in order to understand the variation in the speed of the device for negative and positive photocurrent regimes. As shown in Figure 3c, the fall time (τ_F) remains nearly constant over gate voltage for both 690 (visible) and 840 nm (NIR) illumination. However, we observe that (i) τ_F is lower in the positive I_{ph} regime i.e. under 840 nm illumination compared to 690 nm and (ii) there is a second time constant at $V_G = -2 V$ (~ 1.5 x 10³ sec) which arises from hole trapping in the MoS₂ flake (discussed later in this paper). Under 690 nm illumination, free carriers in both flakes (p_{BP} and n_{M}) are responsible for photoconduction and negative I_{ph} . The slow response of the MoS₂ flake (as can be observed from the slow recovery of the MoS₂ FET after the laser is switched off, shown in Figure S2a of Supporting Information) due to long detrapping time of the photogenerated holes results in increased lifetime of the photogenerated electrons thereby leading to a large τ_F .³³ However, under 840 nm illumination, the positive I_{ph} arises only from the photogenerated carriers of BP thereby resulting in relatively faster optical operation or lower fall time. This can also be observed in Figure 2b where the photocurrent I_{ph} (or photoresponsivity, R) increases in magnitude with each optical cycle under visible light as it is limited by the time constant of the carriers in the MoS₂ flake, however a steady on and off cycles are observed for NIR illumination due to fast hole detrapping time constant in the BP flake. Figure 3d shows variation in τ_F and R with wavelength. For λ < 750 nm, τ_F is higher (~ 55 sec) due to MoS₂-limited dark current recovery. For λ beyond 750 nm, lower fall times are observed due to higher mobility in the BP flake and faster detrapping time for trapped photocarriers from shallow traps in BP bulk.³²

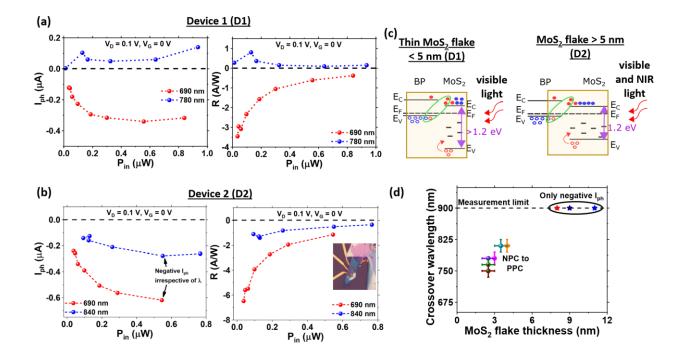


Figure 4: **MoS**₂ **thickness dependent NPC and PPC crossover wavelength**- Photocurrent and responsivity as a function of input laser power for (a) device 1 (MoS₂ thickness of ~3 nm) and (b) device 2 (MoS₂ thickness of 11 nm) under 690 and 840 nm illumination. Negative photocurrent in visible and NIR corroborates absorption of light by both MoS₂ and BP flakes. (c) Band alignment in BP and MoS₂ with varying thickness of MoS₂ flake. (d) MoS₂ thickness vs crossover wavelength, λ_t (wavelength at which the photocurrent transitions from negative to positive values).

MoS₂ Thickness Dependent Negative Photocurrent

The negative photocurrent depends on the free carrier concentrations of BP and MoS₂ flakes that can be modulated in magnitude (photoresponsivity) and spectral range by the gate voltage and the optical absorption range of the MoS₂ flake respectively. Given that light absorption by the MoS₂ flake results in generation of photocarriers that diffuse towards BP resulting in interlayer recombination and hence, negative I_{ph}, the optical spectral response of MoS₂ determines the crossover wavelength from NPC to PPC for the phototransistor. The spectral response of MoS₂ is limited by its bandgap which varies with the thickness of the flake and therefore, the crossover wavelength increases for the first few nanometers of the MoS₂ flake as the bandgap decreases with increasing thickness, till the bandgap becomes constant ($\sim 1.2 \text{ eV}$) for a few layer MoS₂ flake. Figure 4a-c shows the optical response and corresponding band diagrams for two phototransistors with \sim 3 nm and 11 nm thick MoS₂ flakes. Device 1 (flake thickness \sim 3 nm) shows negative (positive) I_{ph} and R for 690 nm (780 nm) as its λ_t is approximately 750 nm (~ 1.65 eV) which is close to the bandgap of the MoS₂ flake. On the other hand, the 11 nm thick MoS_2 flake in device 2 has a bandgap of ~1.2 eV. Hence, it exhibits a negative optical response to both 690 and 840 nm illumination since its λ_t is greater than 1000 nm (which is difficult to demonstrate given the limitation of our measurement setup). As the flake thickness of MoS₂ increases further, the diffusion of electrons from the top surface (high optical absorption region) of the MoS₂ flake towards BP becomes less favorable. This leads to negligible interlayer recombination resulting in a direct flow of electrons from conduction band of MoS_2 to the contacts. This leads to a positive I_{ph} for visible and NIR illumination, as shown in Figure S5 (device 3). It should be noted that a few layer BP flake is selected for these phototransistors with a reasonable Ion/Ioff and a fixed bandgap of ~ 0.3 eV. Figure 4d shows the variation of crossover wavelength with MoS₂ thickness for multiple devices indicating that as the MoS₂ flake thickness increases, λ_t increases till it saturates for few layer flakes.

Applications

The BP/MoS₂ device architecture gives the advantage of switching the photocurrent from negative to positive values within a time scale of a few seconds as the wavelength switches from 700 to 750 nm, as shown in Figure 5a. Photocurrent switching characteristics of two additional devices are shown in Figure S6. This transition can be used in a wavelength dependent multi-bit coding scheme as it helps in differentiating change in current due to different wavelengths of light thereby increasing the accuracy of light recognition. Further, this device also demonstrates negative persistent photoconductance, where the photocurrent reaches a maximum negative value under illumination and when the light is

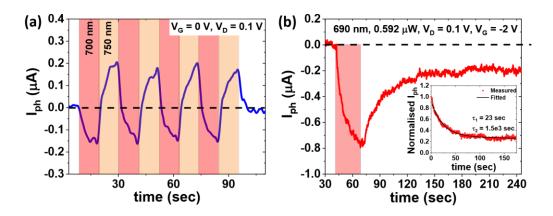


Figure 5: **Wavelength-based photoswitching and negative persistent photoconductance** (a) Wavelength-based photocurrent switching at $V_G = 0$ V and $V_D = 0.1$ V (b) Negative persistent photoconductance at $V_G = -2$ V and $V_D = 0.1$ V with the inset showing a double exponential-based fitting of the normalised photocurrent.

withdrawn, it holds on to a negative current value (lower than the maximum but not the same as the dark current) for a long period of time. Figure 5b shows negative persistent photoconductance of device 1 for $V_G = -2$ V with the normalised photocurrent Y (shown in Fig 5b inset) following a double exponential function: $Y = A_1 exp(-t/\tau 1) + A_2 exp(-t/\tau 2)$.³⁴ Here t is time, A₁ and A₂ are constants and τ_1 and τ_2 are fast and slow decay time constants respectively. The faster time constant, $\tau_1 = 23$ sec symbolises rapid relaxation of the device's photocurrent in response to light withdrawal, whereas the slower time constant $\tau_2 = 1.5 \times 10^3$ sec arises from hole trapping in MoS₂ on visible light illumination which results in slower decay in current. This behavior is similar to the long-term potentiation observed in synaptic devices. Similar behavior for another device (device 6) along with all its other optical measurements is shown in Figure S7.

Conclusions

This work demonstrates wavelength-dependent photoconductance polarity and reversible NPC-PPC switching in a BP/MoS₂ phototransistor. Table 1 compares the key optical characteristics of various architectures and devices using 2D materials that demonstrate negative photoconductance along with the BP/MoS₂ phototransistor reported in this work.

The NPC is a result of recombination between photogenerated electrons in MoS₂ with holes in the BP flake. The NPC-to-PPC crossover wavelength is tunable with the thickness of the MoS₂ flake. MoS₂ thickness modulates its bandgap and optical absorption range thereby resulting in NPC (PPC) for wavelengths within (beyond) the absorption range. The device offers dual fold application: first, different photoelectric response to different wavelengths, owing to the presence of both NPC and PPC in the same device, expands its application prospects to broadband photoelectric sensing and second, the presence of negative persistent photoconductance at negative gate voltage offers a promising avenue for optocontrolled synaptic applications.

Experimental Procedure

The BP transistors were fabricated using a degenerately doped p-type Si substrate with 280 nm thermally grown SiO₂. BP flakes were mechanically exfoliated using scotch tape and transferred onto the substrate. The flakes were then identified using an optical microscope and source/drain contacts (along with an additional adjacent contact) were patterned by electron beam lithography (Raith 150-Two) using poly(methyl methacrylate) resist. Source/drain metal (Cr/Au -5/40 nm) was deposited using sputtering followed by lift-off. Further, MoS₂ flakes were mechanically exfoliated from the molybdenite crystal using polydimethylsiloxane (PDMS) and were transferred on the fabricated BP FET using a pick-and-transfer process using a micromanipulator setup. The contacts on MoS₂ were fabricated using a e-beam lithography and metal deposition. The final device image was taken using a Olympus BX-63 microscope and the SEM imaging was done using Raith 150-Two. ULVAC-PHI/PHI5000 Versa ProbeII focus X-ray photoelectron spectrometer was used for XPS measurements and Horiba HR 800 Raman spectroscopy system with a 532 nm laser was used for Raman imaging. Before optical characterization, the device was placed on a PCB with large gold contact pads. The device contact pads were wire bonded using gold wire to

Ref	Material	Spectral	NPC	NPC ↔ PPC	Mechanism	NPC-to-PPC switching		Application
		response (nm)	and PPC	modulator		Modulator	Reversible	
29	BP	830	only NPC	NIR	bolometric effect			
35	MoS ₂	NIR	only NPC	Monolayer MoS2	trion formation			
36	MoS ₂	454, 519, 625, 980 and 1550	both	NIR	bolometric effect			
18	ReS2/hBN /MoS2	520, 637, 830 and 1310	both	V_G and λ	charge trapping			Photoelectronic memory
19	WS ₂ /RGO	808	only NPC	NIR	recombination			
20	$\frac{\text{BP/}}{\text{SnS}_{0.5}\text{Se}_{1.5}}$	365 and 894.6	both	VG	charge trapping			
21	Gr/BP	655, 785 and 980	both	VG	electron trapping			
22	MoSe ₂ /Gr	450 to 1000	both	VG	charge transfer			
23	Gr/MoS ₂	635	both	VG	charge transfer			
37	MoTe ₂ /Gr	975	both	laser power	charge transfer	laser power	Yes	
This work	BP/MoS ₂	690 to 900	both	$\lambda \sim MoS_2$ bandgap	recombination	λ	Yes	Photoelectronic memory

Table 1: Comparison of this work with previous studies demonstrating negative photoconductance.

the large PCB contact pads. The optoelectronic measurements were done in ambient conditions under a BX-63 Olympus microscope using a Keysight B1500A semiconductor device analyzer using an NKT laser with a wavelength range of 690 to 900 nm. Switching of laser power was done using input of square pulses of 10 V peak-to-peak to the laser power controller unit from an Agilent 33220A function generator. The laser was incident on the device through the objective lens of the BX-63 Olympus microscope.

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Supporting Information Available

The supporting information consists of table with data set of 10 devices, transfer and output characteristics of BP and MoS₂ FETs (device 1), optical characteristics of MoS₂ FET (device 1), optical characteristics of multiple phototransistors (device 1, device 3, device 4, device 5 and device 6).

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Supporting Information

Wavelength-Controlled Photocurrent Polarity Switching in BP-MoS₂ Heterostructure

Himani Jawa,[†] Sayantan Ghosh,[†] Abin Varghese,^{†,‡} Srilagna Sahoo,[†] and Saurabh Lodha^{*,†}

†Department of Electrical Engineering, IIT Bombay, Mumbai, Maharashtra 400076 ‡Department of Materials Science and Engineering, Monash University, Clayton, Victoria,

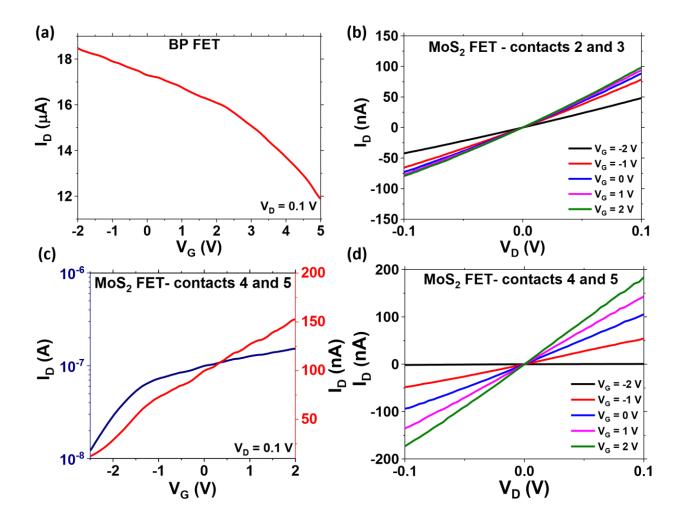
Australia 3800

E-mail: slodha@ee.iitb.ac.in

Details of the Fabricated BP-MoS₂ Phototransistors

Device	MoS2 thickness (nm)	BP thickness (nm)	NPC and PPC
1	~3	21	both
2	11	few layer	only NPC
3	14	8	only PPC
4	~2.5	~9	both
5	~3	~33	both
6	~3.5	15	both
7	8	3	only NPC
8	9	~30	only NPC
9	~ 2.5	few layer	both
10	4	few layer	both

Table S1: MoS₂ and BP thicknesses for the various phototransistors fabricated in this study.



Transfer and Output Characteristics of BP and MoS₂ FETs

Figure S1: (a) Transfer characteristics of the BP FET (b) Output characteristics of the MoS_2 FET between contacts 2 and 3 (contacts are below the MoS_2 flake) (c) Transfer and (d) output characteristics of the MoS_2 FET between contacts 4 and 5 (contacts fabricated on top of the MoS_2 flake).

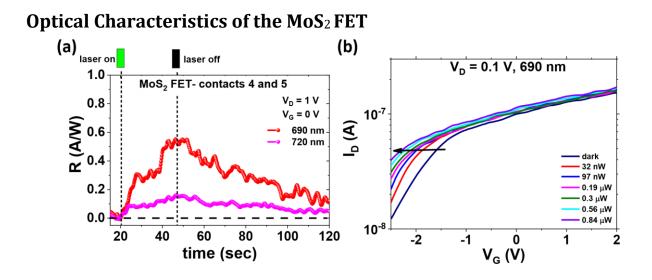
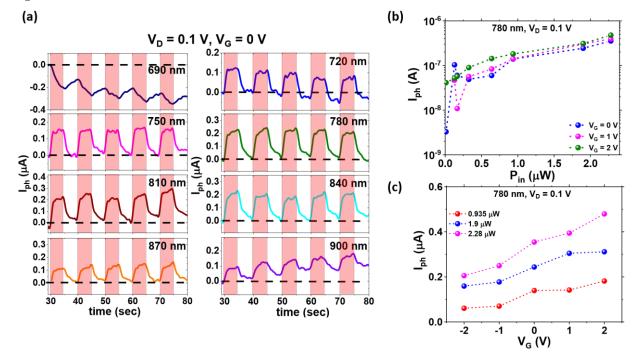


Figure S2: (a) Optical response of the MoS₂ FET under 690 and 720 nm illumination at $V_G = 0$ V and $V_D = 1$ V (b) Transfer characteristics of the MoS₂ FET for varying incident laser power of 690 nm at $V_D = 0.1$ V showing photogating effect due to trapped photogenerated holes.



Optical Characteristics of the BP-MoS₂ Phototransistor

Figure S3: (a) Photoswitching of device 1 for wavelengths ranging from 690 to 900 nm at V_G = 0 V and V_D = 0.1 V (b) Photocurrent vs incident laser power and (c) Variation of photocurrent with gate voltage under 780 nm illumination.

Model for Photocurrent Modulation with Gate Voltage and Laser Power

Under 690 nm illumination, n_M (dotted blue curve) and p_{BP} (dotted red curve), as shown in Figure S4a, are the total electron and hole concentrations at laser power P_{in1} that can be modulated with V_G . Carrier recombination, which determines the I_{ph} , depends on both n_M and p_{BP} resulting in a U-shaped curve (green curve). As the laser power is increased to P_{in2} , under ideal conditions, $n_M \times p_{BP}$ increases, given the increase in the photogenerated carriers (shown by the black curve in Figure S4a). However, due to trapping at the BP/SiO₂ interface, the hole concentration is limited in BP (although photogenerated electrons are available in MoS₂). This results in the left shift of the $n_M \times p_{BP}$ plot and hence, the I_{ph} , with the maximum occurring at negative V_G as shown by the pink curve.

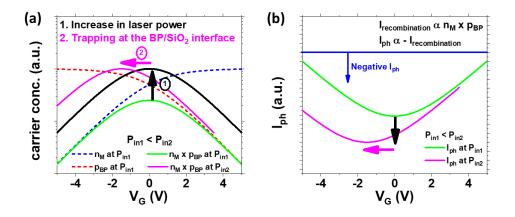


Figure S4: Model for (a) carrier concentration and (b) photocurrent variation in BP/MoS₂ phototransistor with gate voltage and optical power.

Band Alignment and Optical Characteristics of Device 3

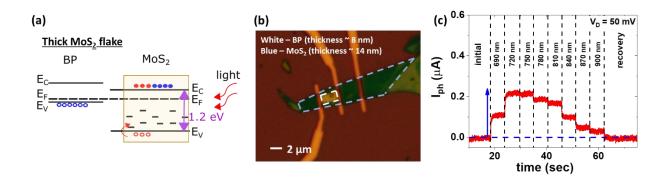


Figure S5: (a) Band alignment between BP and MoS₂ for a thick MoS₂ flake. (b) Optical image of device 3. (c) Photocurrent response of device 3 under different wavelengths showing a positive photocurrent irrespective of the wavelength.

Photoswitching Characteristics of Device 4 and 5

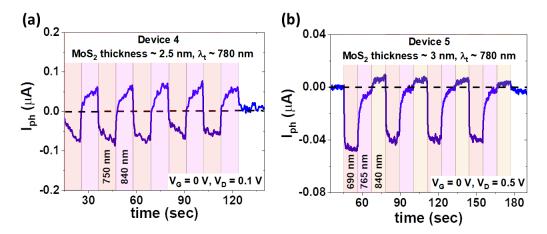


Figure S6: Wavelength-based photoswitching of (a) Device 4 and (b) Device 5.

Optical Characteristics of Device 6

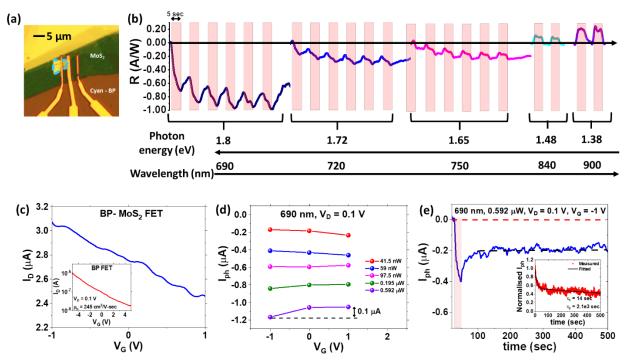


Figure S7: (a) Optical image of device 6 (b) Photoswitching with on and off time being 5 sec at $V_G = 0$ V and $V_D = 0.1$ V for different wavelengths. (c) Transfer characteristics of BP/MoS₂ device with the inset showing the transfer characteristics of the BP FET (d) Variation in photocurrent as a function of gate voltage under 690 nm illumination (e) Negative persistent photoconductance at $V_G = -1$ V and $V_D = 0.1$ V with the inset showing a double exponential-based fitting of the normalised photocurrent.