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Passivated ambipolar black phosphorus transistors†

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We report the first air-passivated ambipolar BP transistor formed by applying benzyl viologen, which serves as a surface charge transfer donor for BP flakes. The passivated BP devices exhibit excellent stability under both an ambient atmosphere and vacuum; their transistor performance is maintained semi-permanently. Unlike their intrinsic p-type properties, passivated BP devices present advantageous ambipolar properties with much higher electron mobility up to $\sim 83 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ from 2-terminal measurement at 300 K, compared to other reported studies on n-type BP transistors. On the basis of the n-type doping effect that originated from benzyl viologen, we also systematically investigated the BP thickness dependence of our devices on electrical properties, in which we found the best electron transport performance to be attained when an $\sim 10 \text{ nm}$ thick BP flake was used.

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Introduction

Since the discovery of graphene, 2D layered materials have been explored for their utility in next-generation electronic devices. Graphene exhibits an extremely high carrier mobility ($>100\,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and a variety of interesting physical properties;^{1–3} however, its zero band gap strongly limits its application to semiconductor electronics. By contrast, transition metal dichalcogenides (TMDCs), such as MoS_2 , WS_2 , *etc.*, possess sizable band gaps and provide high on/off ratios. As a result, TMDCs and their hybrid heterostructures^{4,5} have been investigated for high-performance electronic, optoelectronic, and logical circuit applications. Phosphorene,⁶ with a puckered structure and a one-atom-thick sheet morphology, was recently discovered by isolating the material from layered BP crystals. Unlike graphene and TMDCs, BP has a direct band

gap that increases monotonically from 0.3 eV in bulk to 1.7 eV in phosphorene.^{7,8} These properties, together with a remarkably high hole mobility of $1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and an on/off ratio of 10^5 at room temperature,⁹ make BP suitable for semiconductor applications such as photodetectors,¹⁰ solar cells,¹¹ and digital electronics.¹²

However, two key issues of BP are yet to be solved. On the one hand, the availability of only p-type semiconductor characteristics in BP devices^{13,14} complicates the use of BP alone in complementary logic circuits. The need for symmetric charge transport materials has posed a serious bottleneck in complementary metal–oxide–semiconductor (CMOS) application, in which n-type transistors are required to reduce static power consumption in logical circuits and systems. It is reported that BP transistors display unipolar and ambipolar behaviors, *via* contact-metal engineering with lower work function.^{15,16} Ambipolar BP FETs obtained from capping of dielectric materials, such as Al_2O_3 , h-BN and graphene, have also been reported recently.¹⁷ In order to achieve the electron- and hole-doping effect, Xiang *et al.* modulated the surface of BP *via* depositing Cs_2CO_3 and MoO_3 layers.¹⁴ On the other hand, BP-based devices are still subjected to degradation after a short exposure to air.^{13,18} Li *et al.* demonstrated significantly improved air stability in ionophore coated BP FETs.¹⁹ In addition, encapsulation with h-BN and graphene has been studied.^{16,17} Nevertheless, these approaches are not suitable for logical applications because these protective layers render BP to be limited only to show p-type semiconductor characteristics while ambipolar BP with acceptable air stability is required.

In this work, we report an effective method for passivating few-layer BP field-effect transistors (FETs) with excellent

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†Electronic supplementary information (ESI) available: Transfer characteristics of BP field effect transistors (BV1–BV4) (Fig. S1 and S2 and Table S1); output characteristics of BP field effect transistors in different directions (Fig. S3). Performance characteristics of the recent work (Table S2). N-type BP FETs (Fig. S4). Output characteristics of BV passivated BP field effect transistors after exposing to air for 180 days (Fig. S5). The relationship between temperature (T), BV reduction potential (ΔE_{R}) and Fermi level change (ΔE_{F}) (Fig. S6). Air-stable characteristics vs. time (Table S3). The inverter characteristics of the BP device (Fig. S7). Capping BP using h-BN (Fig. S8 and S9 and Table S4). See DOI: 10.1039/c6nr02554d

stability under both an ambient atmosphere and vacuum *via* benzyl viologen (BV) doping. More importantly, the thus produced BP devices show ambipolar properties, converted from their pristine p-type properties. Our findings demonstrate that BP can be a robust material for use in future high-efficiency optoelectronic and logical electronic applications.

Results and discussion

Chemical doping of BP using BV

The use of BV as a simple and effective chemical doping approach can greatly enhance the electron concentration in 2D materials, similar to graphene²⁰ and MoS₂.²¹ Surface charge transfer doping has been accomplished by various methods for various applications.^{20,21} Fig. 1a shows schematic diagrams of BP FETs fabricated using our method (see the Methods section for details). After the BP FET devices were fabricated, BV was spin-coated onto the BP surface in a glove box purged with argon. The samples were then heated at 100 °C to evaporate the solvent and induce electron doping. Fig. 1c shows a schematic diagram of a BP device prepared with BV treatment. An optical microscopy image of a few-layer BP FET is shown in Fig. 1b. An exfoliated few-layer BP was confirmed by the Raman spectra shown in Fig. 1d, in which the signature BP peaks were observed at 364, 438, and 465 cm⁻¹, corresponding to the three vibrational modes (A_g¹, B_{2g}, and A_g², respectively) of the BP crystal lattice.^{22,23} Note that the Raman spectra of the BP layer were obtained after completing the device fabrication process including the chemical doping step and the electrical (photoresponse) measurements, to prevent BP from being damaged under the Raman laser illumination. According to Fig. 1d, we can confirm that our BP in the device structure retains its inherent material properties even after undergoing the FET processing.

We firstly fabricated 2-terminal configuration structured devices to see the BV doping effect of BP FETs. Fig. 1e shows the typical output characteristics of a fabricated pristine BP FET (BV1 as the device with 8 nm thick BP, here BV# denotes a BP FET fabricated by BV doping) at various gate voltages (V_{gs}) under vacuum at 300 K. The excellent linearity of the curves indicates the Ohmic contact between the metal (Ti/Au = 20/50 nm) and the few-layer BP. In this work, all BP flakes were exfoliated in a glove box, and coated with methyl methacrylate (PMMA) also in a glove box to avoid unwanted reactions with air during device fabrication. Fig. 1f shows the transfer characteristics of a BP device (BV1) before and after BV doping. The ambipolar behavior of the device could be clearly observed after chemical doping using BV. Application of V_{gs} between -40 and 40 V increased the source-drain current (I_{ds}), as shown in the red curve at $V_{ds} = 1$ V, along both the negative and positive sweep directions, indicating hole and electron transport. In addition, Fig. S1a and S1b† show the good conductance of BV1 under p- and n-type operations, respectively. Here, the mechanism of BV doping to our BP devices is explained by the changes of the Fermi level. Fig. S1d† shows

the small band gap of the few-layer BP, 0.3–0.5 eV,⁷ and the band diagrams of BP devices at equilibrium where BP transistors always show p-type behavior. In this case, the BV dopant on the BP surface serves as an electron donor that tunes the Fermi level of BP to produce ambipolar BP FETs. That is, as a result of doping, the Fermi level was dragged toward higher energies, to the conduction band, which enhanced electron transport and reduced hole transport.

The chemical doping effects of BV were confirmed from all the tested devices (see Fig. S1 and S2†). All the devices displayed clear ambipolar behavior. Table S1† lists the key figures of merit used to benchmark the performances of the pristine and BV-doped BP devices. The field effect carrier mobility (μ) was calculated according to the equation: $\mu = (1/C_{ox}) \times (dI_{ds}/dV_g) \times (L_{ch}/W_{ch})/V_{ds}$, where $C_{ox} = 1.15 \times 10^{-8}$ F cm⁻² for 300 nm SiO₂, L_{ch} is the channel length, and W_{ch} is the channel width. We obtained an electron mobility of 83 cm² V⁻¹ s⁻¹ after BV doping, by using BV3 with a 10 nm thick BP (see Table S1,† Fig. 4). Note that the mobilities shown in the table are obtained from 2-terminal measurements, which means the true channel properties of our doped BP should be better, considering that the contact resistance between BP and metal is significant. It is known that the effective mass plays an important role in anisotropic layered materials, *e.g.* BP¹¹ in which the electron mobility can be higher along the *x*-direction of the BP channel. We fabricated two devices to investigate the properties of the anisotropy in BP. Fig. S3† shows the anisotropy in mobility (μ) in BP. It can be seen that the electron transport along the *x*-direction is higher than the *y*-direction, because of the different effective mass. In order to confirm the effectiveness of our doping process, Table S2† compares the ambipolar device performances of the BP FETs fabricated by various research groups. The performance results reported here were much better than the performances reported in previous devices,^{14,16,24–28} indicating that chemical doping using BV is an effective method for improving electron transport in BP devices.

Air-passivated n-type BP FETs

Furthermore, we used BV to dope both the channel part of BP and the parts under the metal to convert p-type dominant BP transistors to ambipolar. Fig. 2a shows the electrical transfer properties of fully covered BP FETs. The insets show schematic diagrams and optical microscopy image of the device. The high performance n-type behavior of the device is clearly observed, indicating electron transport dominant BP FETs (the results from other examples are found in Fig. S4†). In addition, I_{ds} shows electron current saturation behavior at high positive V_{gs} , indicating the formation of good contact between metal and BP. To elucidate this behavior, charge transport measurements of BP-FETs are performed by using both 2-terminal and 4-terminal device configurations to separate contact and channel properties of BP-FETs. A four point measurement technique was used to extract the contact resistance *via* $R_c = (R_{2P} - R_{4P} \times (L_{2P}/L_{4P})) \times W/2$, where R_c is the contact resistance, R_{2P} is the 2-terminal resistance, R_{4P} is the 4-terminal

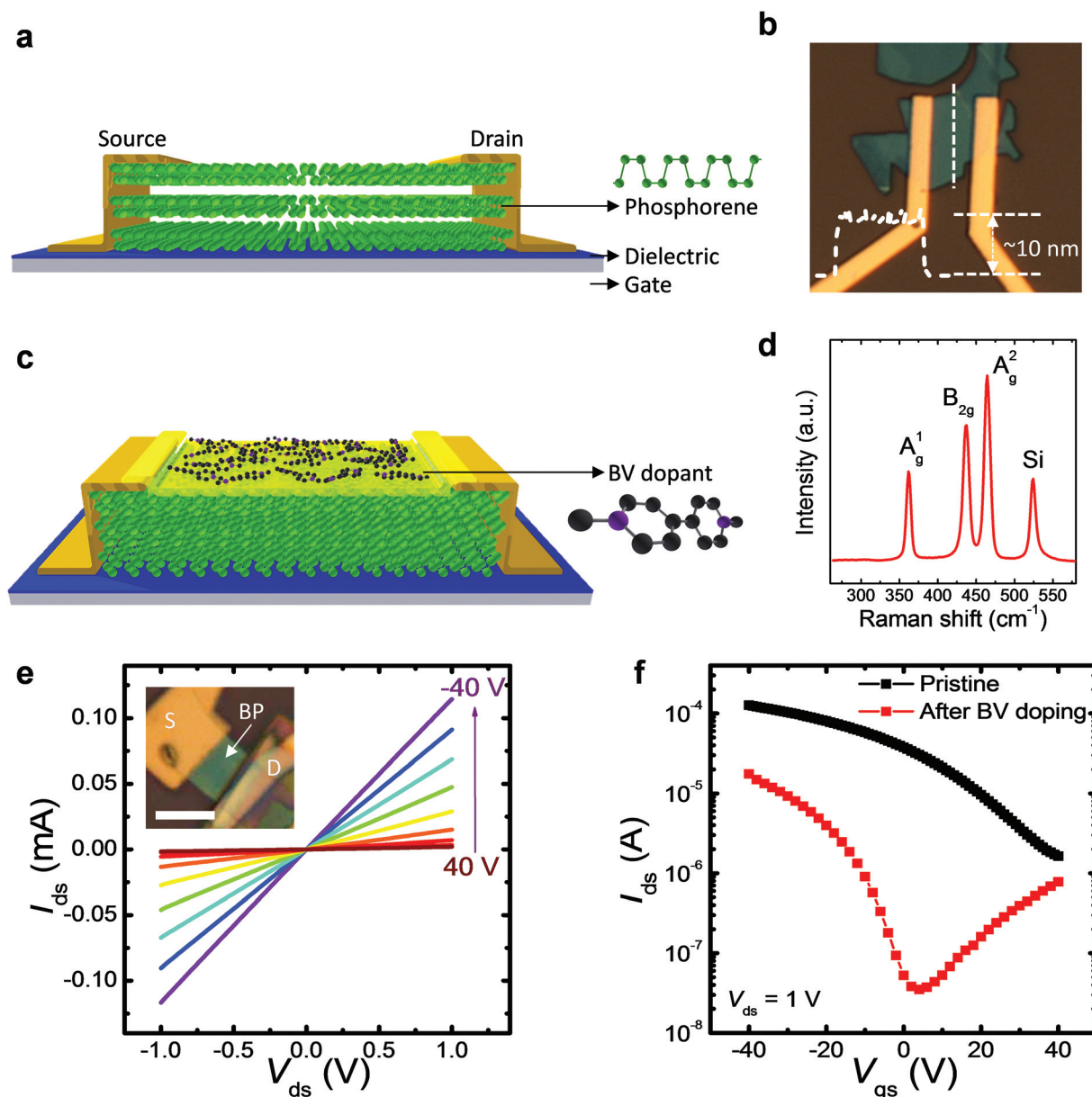


Fig. 1 BP devices used in this study. (a) Schematic diagram showing the BP (green color) FET. 20/50 nm thick Ti/Au was used as the source and drain contacts (yellow color), and the Si substrate was covered with a 285 nm thick SiO₂ (blue and grey color) as a global back gate. (b) Optical microscopy image of representative BP FET used in this study. The AFM profile along the dashed line is shown in the photograph. The scale bar indicates 10 μm . (c) BV-doped BP FET. The yellow layer is the chemically doped layer. The structure of the BV dopant is shown schematically on the right. (d) Raman spectra of the BP used in this study. The A_g^1 , B_{2g} , and A_g^2 peaks were obtained from measurements of the BP layer. (e) Output curves obtained from the pristine BP device as a function of the gate bias. The clear linearity of the curves indicated the Ohmic contact at the interface between the metal and the BP layer. The inset shows an OM image of the device. The scale bar indicates 5 μm . (f) Transfer curves obtained from the pristine, BV-doped BP devices. Ambipolar carrier transport was observed after chemical doping.

resistance, L_{2p} and L_{4p} are the lengths of 2 probe and 4 probe channels respectively, and W is the contact width. The inset image in Fig. 2a shows the BP transistor array consisting of 7 transistors which is formed after BV passivation and metal deposition. Fig. S4b† shows the contact resistance as a function of V_{gs} in p- and n-type operations.

The air-passivated properties of BP transistors can be maintained in air for as long as 250 hours due to the formation of

the protective layer of the BV dopant, as seen in Fig. 2b. Here, we first demonstrate that the BV dopant layer can be used for passivation of BP. Furthermore, we analyze maximum mobility ($\mu_{n, \text{max}}$) and saturation current in both p-branch and n-branch of BP transistors. Fig. 2c shows the maximum mobility vs. time in both p-branch and n-branch, in which hole mobility can sustain steadily for a long period, however, electron mobility shows a slight decrease. This confirms that the BV dopant can

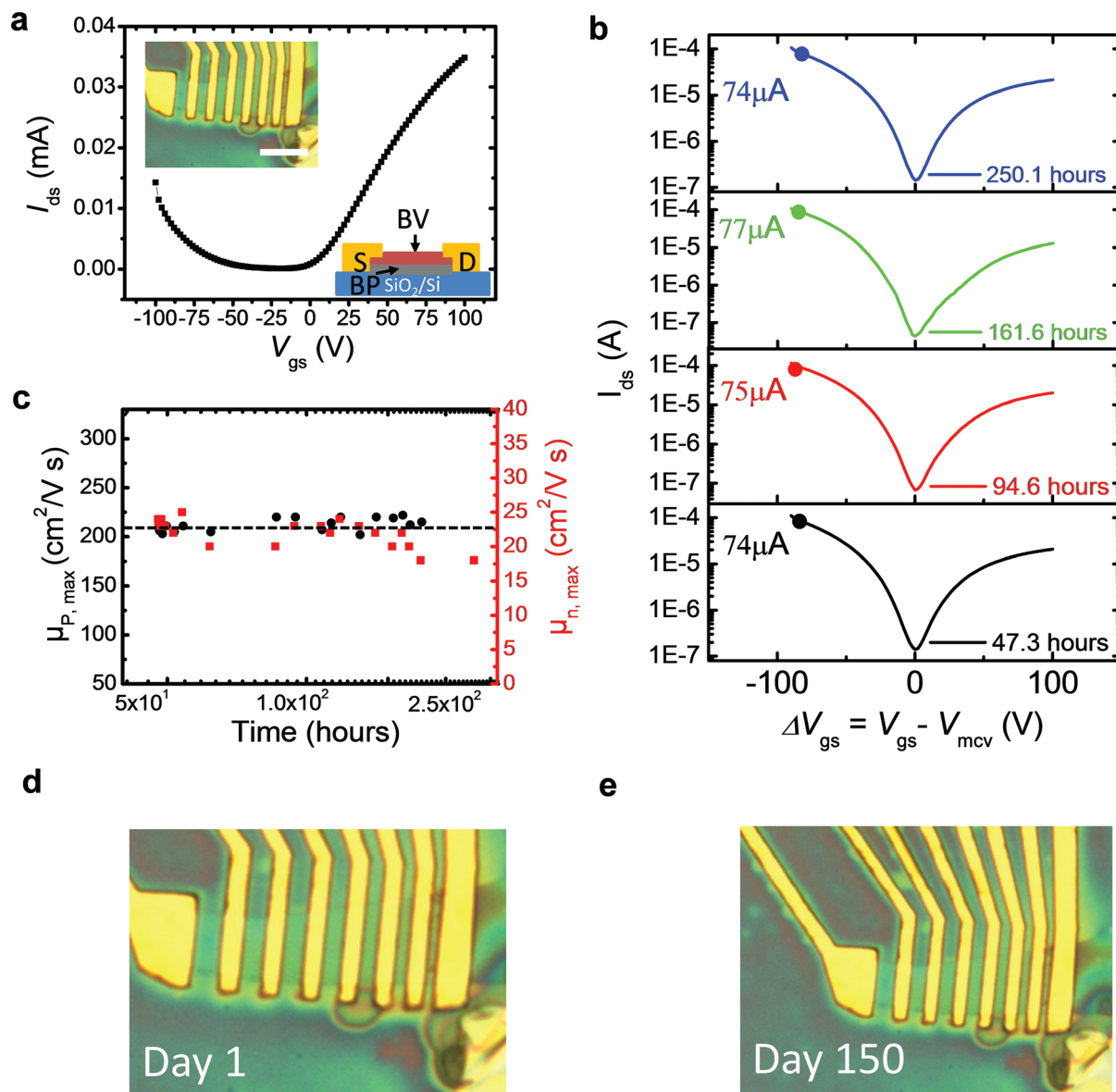


Fig. 2 Passivated n-type BP FETs. (a) Transfer curves obtained from the BP devices doped and covered by BV. N-type carrier transport was observed after chemical doping. The insets show schematic diagrams and optical microscopy image of the device. The scale bar indicates 5 μm . (b) Air-stability of the passivated BP devices, which was kept in air as long as 250 hours at $V_{\text{DS}} = 0.5$ V. V_{mcv} is the minimum-current value. (c) $\mu_{\text{p,max}}$ is the maximum mobility for holes, and $\mu_{\text{n,max}}$ is the maximum mobility for electrons. High hole mobility is sustained semi-permanently. (d, e) Optical images of a BP passivated with BV on day 1 and day 150, respectively, demonstrating no obvious optical evidence for degradation.

form a protective layer on the BP surface to prevent ambient chemicals, such as O_2 and H_2O , from reacting with it, so as not to degrade our BP devices. That is, we demonstrate that our n-type BP devices exhibit excellent stability under both an ambient atmosphere and vacuum, which can maintain its n-type performance for long period and its p-type performance near permanently, due to the passivation effect of BV on BP. The detailed analysis data are shown in Table S3.†

The effect of temperature on ambipolar properties of BP devices

To further understand the properties of our ambipolar BP FETs, we investigated the influence of temperature.

Compared to other organic molecules, BV has a very low reduction potential, making it to be an effective donor.²⁹ Fig. 3a shows the change of electric transfer characteristics in BV-doped BP devices. From the curves, it can be clearly seen that the minimum current (I_{min}) shifted towards the high V_{gs} with the temperature decrease, which means the devices convert from ambipolar to p-type. The reason for the conversion can be interpreted by using BV reduction potential. Fig. S5a† shows the expected energy level offset between the conduction band edge of BP and the reduction potential of the BV molecule. It can be concluded from the literature that bulk BP has a conduction band edge at ~ 0 V vs.

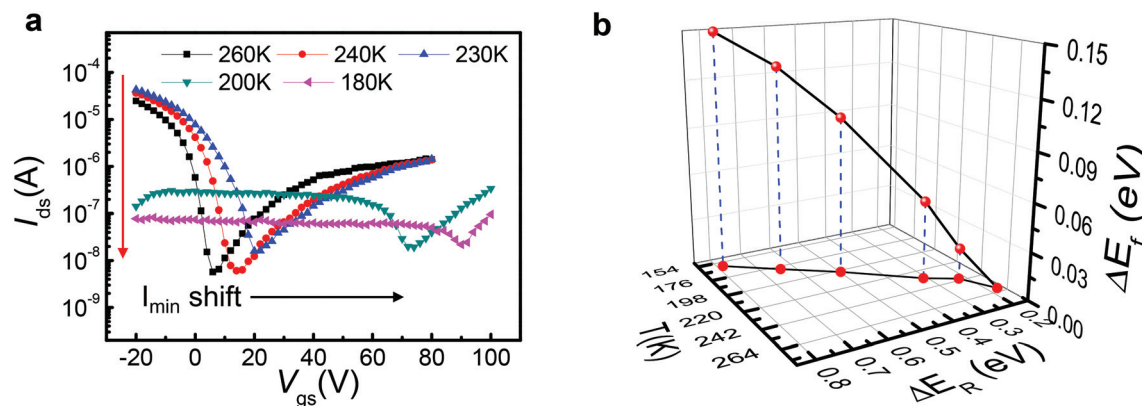


Fig. 3 Effect of temperature on the ambipolar properties of BP devices. (a) Transfer curves of the BV-doped device obtained at different temperatures. (b) The relation between temperature (T), BV reduction potential (ΔE_R) and Fermi level change (ΔE_f).

the standard hydrogen electrode (SHE)^{7,29–31} while the reduction potentials of the BV molecule are $E_1 = -0.79$ V (BV^0/BV^1) and $E_2 = -0.33$ V (BV^+/BV^{2+}).^{29,31} Because of this energy level offset, BP and BV act as electron-acceptor and -donor materials, respectively. So, the BV^0 molecule can readily transfer electrons to BP. When the temperature decreases, ΔE_R (variation of BV reduction potential) increases which means BV becomes an ineffective chemical, corresponding to Fig. 3a, resulting in a Fermi level change. It is understood that ΔE_R is highly dependent on the temperature (T). Moreover, bulk BP has a small band gap, indicating that its polarity can be sensitively affected by the change of ΔE_R . For the reactions: $BV^{2+} \rightleftharpoons BV^+ \rightleftharpoons BV^0$, the first reduction step is highly reversible and can be cycled many times without a significant side reaction.³¹ As the temperature decreases, ΔE_R shifts down and the BV dopant becomes ineffective, which is corresponding to the electrical performance shown in Fig. 3a, resulting in our BP device showing stronger p-type behavior at lower temperature. Based on our experimental results, we found that the relation between temperature, BV reduction potential and Fermi level change obeys $\Delta E_R/E_0 = 0.39 \log(\Delta V)$, where $\Delta V/V_0 = 4 \exp(\Delta E_f/kT)$, ΔE_R is the variation of BV reduction potential, E_0 is the original reduction potential, ΔV is the gate voltage corresponding to the minimum I_{ds} current, V_0 is the voltage corresponding to the minimum I_{ds} current at room temperature, $\Delta E_f = (E_i - E_0)$ is the Fermi level variation, k is the Boltzmann constant, and T is the temperature. Here, we set $E_0 = 0.33$ V and $V_0 = 5$ V. Then, we plotted Fig. 3b based on this simulation. From the curve, we can find that when the temperature decreases, ΔE_R increases which means BV becomes inactive corresponding to Fig. S6a,[†] resulting in the increase of the Fermi level change. Note that, the current level with the decreasing temperature becomes lower than the pristine state as shown in Fig. 3a with the red arrow, due to the ineffective BV dopant layer at the lowered temperature inducing scattering on the surface of BP. We found that the BV doping is effective in the temperature range $> \sim 150$ K in our BP devices.

BP thickness dependence of BV-doped devices

We next investigated the flake thickness dependence of electron transport after BV doping. We used atomic force microscopy (AFM) to measure the thickness of our BP flakes. Even though AFM is not an ideal method for determining the precise number of BP layers, it can present general trends related to transport properties in the devices, which can be determined by the relative differences in thickness on the substrate. The thickness dependence of electron mobility is depicted in Fig. 4, where our doping is found most effective for ~ 10 nm BP flakes. Considering the anisotropic properties of BP, we used the statistical data of our devices to obtain the thickness dependence of our passivated BP FETs. With different layer thicknesses ranging from ~ 6 to ~ 18 nm, we can observe that the electron mobility increases as the layer thickness increases while it decreases when $> \sim 10$ nm. The non-monotonic trend of the electron mobility can be easily explained using a resistive network model comprised of Thomas–Fermi charge screening and interlayer resistive

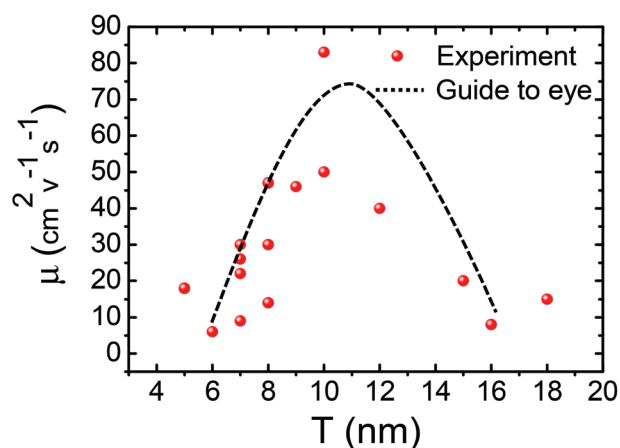


Fig. 4 Dependence of thickness on ambipolar properties of BP devices. Electron mobility (μ) vs. layer thickness (T) obtained from our BV-doped devices.

coupling employed for multilayer MoS₂ and BP systems.^{8,32,33} In general, the use of an optimum number of BP layers is necessary for attaining high electron mobility since the impact of the substrate on the device performance can be eliminated. The highest electron mobility was extracted to be 83 cm² V⁻¹ s⁻¹ for a ~10 nm thick flake according to the two-terminal measurement. Under any given V_{gs} , the current can easily flow through the upper layers. When the thickness of BP is smaller than a critical point (10 nm in our experiments), the current can easily flow through all the layers (upper layers). But, if the thickness of BP is too large, there involves the interlayer resistance which impedes the current to flow in the lower layers. So, the current will not monotonically increase as the thickness increases, which is consistent with our results shown in Fig. 4.

Homogeneous BP inverter

While we succeeded in BV doping to obtain ambipolar BP FETs, we additionally employed h-BN masking to encapsulate BP FETs to convert few-layer BP field-effect transistors (FETs) from p-type to ambipolar. Capping BP using transparent h-BN effectively improved electron transport in BP devices relative to other techniques^{14,16,24–26} by screening the hole charge transport induced in an air environment. These effects rendered BP suitable for transparent photodetector and logical circuit applications (see ESI Note 1 for the details on h-BN capping and Fig. S8†).

Using the above techniques, we fabricated a logical inverter using homogeneous BP that was treated differently for two regions. Unlike previous studies,^{12,34,35} the inverter was based on homogeneous BP that had been doped with BV for one region and capped with h-BN for the other region. The inset in Fig. 5 illustrates an inverter fabricated using a few-layer BP. V_{IN} is the input voltage, V_{OUT} is the output voltage, and V_{DD} is the supply voltage. The use of the two different methods yielded two different ambipolar BP device states. The Fermi level of

h-BN capped BP FETs is nearer to the conduction band edge when comparing to the BV doped part. Therefore, the h-BN capped and BV doped BP transistors served as n- and p-type transistors in the inverter, respectively. We grounded the electrode of the h-BN capped BP part as shown in the inset of Fig. 5. When applying the forward V_{gs} , the electrons flowed easily from the grounded electrodes, which became low input. By contrast, when applying the backward V_{gs} , the h-BN capped BP transistor was off, and the holes can flow easily from the BV doped part, which became high output. The main panel of Fig. 5 shows the inverter characteristics for the prepared BP devices. In the region in which V_{OUT} was relatively high, V_{IN} was low (as shown in yellow), and *vice versa* (as shown in blue). More inverter characteristics were measured under different V_{DD} values, as shown in Fig. S7a and S7b.†

Conclusion

We report passivated ambipolar BP devices fabricated by a novel method: chemical passivation using BV. Our devices exhibited ambipolar characteristics with an electron mobility of 83 cm² V⁻¹ s⁻¹ at room temperature. The highest electron transport performance was observed from the device with ~10 nm thick BP at 300 K. The mechanism underlying the efficient ambipolar carrier transport was thought to be derived from the control over the Fermi level of BP. Furthermore, we fabricated a logical inverter based on homogeneous BP in which a part of the BP material was doped with BV and the other part was capped with h-BN. Our results demonstrated that BV doping and passivation are very effective in enhancing electron transport and also air stability of BP transistors.

Methods

First, we exfoliated few-layer BP flakes from bulk BP crystals using the Scotch tape and transferred them onto a highly p-type-doped silicon substrate capped with a 300 nm SiO₂ layer under an Ar atmosphere in a glove box. As an EBL pattern mask, PMMA was immediately spin-coated onto the samples to protect the flakes from reacting with air. EBL patterns were generated for the samples, and Ti/Au layers were deposited (20 nm/50 nm). The samples after the lift-off step are shown in Fig. 1a. Chemically doped BP, using BV (40 mM), is illustrated in Fig. 1b. A transparent h-BN capping was also applied to BP, as shown in Fig. S7a.† The electrical performances of the devices were measured using a probe station under vacuum and a semiconductor parameter analyzer (Agilent 4155C).

Acknowledgements

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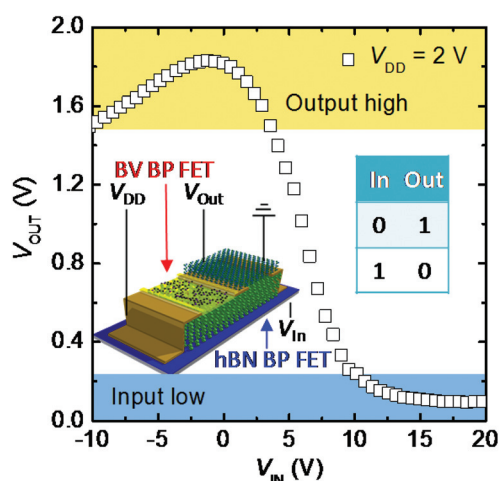


Fig. 5 Homogeneous BP inverter. The output voltage as a function of the input voltage. The hBN-capped and BV-doped devices were linked in series. The insets show schematic diagrams of the device and an inverter logic table.

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