**2D** Phosphorene



# 2D Phosphorene: Epitaxial Growth and Interface Engineering for Electronic Devices

Jia Lin Zhang, Cheng Han, Zehua Hu, Li Wang, Lei Liu, Andrew T. S. Wee, and Wei Chen\*

Black phosphorus (BP), first synthesized in 1914 and rediscovered as a new member of the family of 2D materials in 2014, combines many extraordinary properties of graphene and transition-metal dichalcogenides, such as high charge-carrier mobility, and a tunable direct bandgap. In addition, it displays other distinguishing properties, e.g., ambipolar transport and highly anisotropic properties. The successful application of BP in electronic and optoelectronic devices has stimulated significant research interest in other allotropes and alloys of 2D phosphorene, a class of 2D materials consisting of elemental phosphorus. As an atomically thin sheet, the various interfaces presented in 2D phosphorene (substrate/phosphorene, electrode/phosphorene, dielectric/phosphorene, atmosphere/phosphorene) play dominant roles in its bottom-up synthesis, and determine several key characteristics for the devices, such as carrier injection, carrier transport, carrier concentration, and device stability. The rational design/engineering of interfaces provides an effective way to manipulate the growth of 2D phosphorene, and modulate its electronic and optoelectronic properties to realize high-performance multifunctional devices. Here, recent progress of the interface engineering of 2D phosphorene is highlighted, including the epitaxial growth of single-layer blue phosphorus on different substrates, surface functionalization of BP for high-performance complementary devices, and the investigation of the BP degradation mechanism in ambient air.

## silicon-based electronic devices.<sup>[1]</sup> They can be either isolated from naturally existing bulk materials or synthesized by bottom-up techniques for those without a bulk counterpart.<sup>[2]</sup> Graphene, the forefather of 2D materials, possesses extremely high charge-carrier mobility and a wealth of extraordinary mechanical, thermal, and electronic properties.<sup>[3]</sup> However, the lack of a sizable bandgap limits the application of graphene in logic electronics. Transition-metal dichalcogenides (TMDs) are a class of semiconducting 2D materials distinguished by an intrinsic thicknessdependent bandgap (≈1-2 eV), featuring unique fundamental properties and versatile device applications.<sup>[4]</sup> However, the limited charge-carrier mobility and directto-indirect bandgap transition occurring in most TMDs seriously restricts the device performance in TMD-based electronics and optoelectronics.

Black phosphorus (BP), an allotrope of elemental phosphorus in group V, was first synthesized in  $1914^{[5]}$  and was recently rediscovered as an exciting member in the 2D family.<sup>[6]</sup> The emer-

# 1. Introduction

Over the past decade, 2D layered materials have become a new platform to explore fundamental physics and overcome technological bottlenecks such as scaling limits in conventional

Dr. J. L. Zhang, Prof. W. Chen Department of Chemistry National University of Singapore 3 Science Drive 3, 117543 Singapore E-mail: phycw@nus.edu.sg Dr. C. Han, Prof. W. Chen SZU-NUS Collaborative Innovation Center for Optoelectronic Science and Technology Shenzhen University Shenzhen 518060, China Dr. C. Han, Z. Hu, Prof. A. T. S. Wee, Prof. W. Chen Department of Physics National University of Singapore 2 Science Drive 3, 117542 Singapore

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adma.201802207.

DOI: 10.1002/adma.201802207

gence of BP bridges the gap between graphene and TMDs due to its high carrier mobility and moderate bandgap,<sup>[6a,c,7]</sup> and further opens up the exploration of a class of novel 2D materials composed of phosphorus atoms, namely 2D phosphorene, from bottom-up synthesis to potential applications. Besides

# Prof. L. Wang

Institute for Advanced Study and Department of Physics Nanchang University 999 Xue Fu Da Dao, Nanchang 330031, China Prof. L. Liu State Key Laboratory of Luminescence and Applications Changchun Institute of Optics Fine Mechanics and Physics Chinese Academy of Sciences No. 3888 Dongnanhu Road, Changchun 130033, China Prof. W. Chen National University of Singapore (Suzhou) Research Institute 377 Lin Quan Street, Suzhou Industrial Park, Jiang Su 215123, China



BP, many other phosphorus allotropes with layered structure phases have been proposed by theoretical calculations. Some of them adopt the buckled honeycomb lattice, e.g.,  $\beta$ -P (blue phosphorus, indirect bandgap  $\approx 2 \text{ eV}$ ,<sup>[8]</sup>  $\gamma P$  (indirect bandgap of 0.5 eV),<sup>[9]</sup>  $\delta$ -P (direct bandgap of 0.45 eV),<sup>[9]</sup>  $\lambda$ -P (green phosphorus, direct bandgap of 2.4 eV),<sup>[10]</sup> and red phosphorene (indirect bandgap of 1.96 eV),<sup>[11]</sup> and are nearly equally stable as BP with cohesive energy difference smaller than 0.1 eV. Other nonhoneycomb structures have also been predicted, including single-layer violet phosphorus (direct bandgap of 2.5 eV, high mobility 3000–7000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>),<sup>[12]</sup> phosphorus allotropes composed of P<sub>4</sub> square and P<sub>5</sub> pentagon units,<sup>[13]</sup> porous phosphorus polymorphs (tunable bandgap of 0.15–3.42 eV),<sup>[14]</sup> Ψ-P (indirect bandgap 1.57 eV),<sup>[15]</sup> kagome phosphorus (indirect bandgap of 1.64 eV),<sup>[16]</sup> and two- and fourfold coordinated phosphorus allotropes.<sup>[17]</sup> As a representative in the class of 2D phosphorene materials, BP has a direct bandgap for all numbers of layers, which is tunable from 0.3 eV for the bulk to 2 eV for a monolayer, making it ideal for optoelectronic applications such as broadband photodetection.<sup>[18]</sup> This inherent sizeable bandgap enables BP to be configured as field-effect transistor (FET) devices, showing a high carrier mobility of up to 6000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, current on/off ratio of  $\approx 10^4$ –10<sup>5</sup>, and clear ambipolar transport characteristics, enabling potential applications in complementary logic electronics.<sup>[19]</sup> In addition, BP has also been demonstrated to be a promising candidate for radiofrequency transistors,<sup>[20]</sup> memory devices,<sup>[21]</sup> gas sensors,<sup>[22]</sup> solar cells,<sup>[23]</sup> batteries,<sup>[24]</sup> and so on. Despite the considerable potential of BP, there are still many bottlenecks and challenges that need to be addressed: (1) the synthesis of large-scale and high-quality BP nanosheets is still absent, which limits the large-scale production of BP-based integrated logic devices;<sup>[25]</sup> (2) BP generally shows an unbalanced hole-dominated transport behavior,<sup>[26]</sup> hence restricting its applications in complementary electronics; and (3) the atomically thin BP sheets degrade very fast in ambient air, thus resulting in poor air stability of its device performance.<sup>[27]</sup> All of these limitations necessitate the synthesis of novel 2D phosphorene materials with superior properties, as well as the development of effective schemes to either modulate the electronic properties of 2D phosphorene or protect it from degradation in air.

Similar to other 2D materials, 2D phosphorene is essentially an "interface type" material where the synthesis process, as well as device performance of 2D phosphorene are determined and controlled by the interfaces. First, interfacial interaction between 2D phosphorene and the substrate plays a dominant role in 2D phosphorene bottom-up growth on a specific substrate.<sup>[25]</sup> Appropriate engineering of the substrate toward moderate interfacial interactions, proper symmetry, and matched lattice constant is highly desired for the growth of 2D phosphorene. Second, the electronic properties and device performance of 2D phosphorene are also dominated by the device interfaces. The important device interfaces include the adsorbate/phosphorene, metal/phosphorene, and dielectric/phosphorene interfaces.<sup>[28]</sup> Surface functionalization by coating a specific adlayer on 2D phosphorene offers the opportunity to dope 2D phosphorene effectively, as well as tune its transport properties, hence facilitating complementary device applications.<sup>[29]</sup> Third, the degradation of 2D





Jia Lin Zhang is currently a research fellow in Chemistry Department at the National University of Singapore (NUS). She received her bachelor's degree in physics from Sichuan University (China) in 2010 and her Ph.D. degree from the Physics Department at NUS in 2014. Her current research interests include molecular-scale

interface engineering for optimizing molecular, organic and 2D electronics, and CVD/MBE growth of 2D materials.



**Cheng Han** is currently an assistant professor of Shenzhen University (SZU, China). He received his bachelor's degree in physics from Sichuan University (SCU, China) in 2009 and his Ph.D. degree in physics from the National University of Singapore (NUS, Singapore) in 2014. He did research as a postdoctoral fellow in the

Chemistry Department, National University of Singapore from 2014 to 2017. His research interests mainly focus on interface engineering on novel materials-based functional devices, especially for low-dimensional materials.



Wei Chen is currently an associate professor in both the Chemistry Department and Physics Department at the National University of Singapore (NUS). He received his bachelor's degree in chemistry from Nanjing University (China) in 2001 and his Ph.D. degree from the Chemistry Department at NUS in 2004. His cur-

rent research interests include molecular-scale interface engineering for organic-, graphene-, and 2D-material-based electronics and optoelectronics, and interface-controlled nanocatalysis for energy and environmental research.

phosphorene in air essentially originates from the chemical reaction occurring at the air/2D phosphorene interface. Investigations of the interfacial interactions between 2D phosphorene and air contribute to our understanding of the underlying degradation mechanism, and further enable the development of effective passivation methods to protect 2D phosphorene.<sup>[19b,27,30]</sup>





The aim here is to highlight our recent progress on the interface engineering of 2D phosphorene for epitaxial growth and electronic devices. We begin with a comprehensive overview of recent theoretical advances on the prediction of new phosphorus structures and growth mechanism on different substrates, followed by our experimental investigation of the epitaxial growth of single-layer blue phosphorus on clean and tellurium-functionalized Au(111). Subsequently, we demonstrate the realization of high-performance BP-based complementary devices via the in situ surface functionalization with cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>) and potassium (K), where BP was found to be strongly n-doped with remarkably enhanced electron mobility through surface transfer doping. After that, we present our in-depth exploration of the degradation mechanism of BP under a well-controlled environment. Two degradation channels, the light-induced oxidation in pure oxygen and water-catalyzed oxidation in dark environment are demonstrated. Finally, challenges and opportunities for the interface-engineered epitaxial growth and electronic devices of 2D phosphorene are highlighted.

# 2. Epitaxial Growth of 2D Phosphorene

Elemental phosphorus exists in nature in the form of many allotropes, including white, red, violet (Hittorf), and black phosphorus.<sup>[7a]</sup> Among them, BP is the thermodynamically most stable form under ambient conditions. Although the first discovery of BP can be traced back to a century ago in 1914, the isolation of few-layer BP and the exploration of its device application is a much more recent advance.<sup>[6c]</sup> Its successful demonstration in electronic applications has led to considerable interest to search for new phosphorus structures with complementary properties. Through theoretical calculations, 2D phosphorene allotropes with a variety of atomic structures and electronic properties have been proposed, such as honeycomb  $\beta$ -P (blue),<sup>[8]</sup>  $\gamma$ -P,<sup>[9]</sup>  $\delta$ -P,<sup>[9]</sup>  $\lambda$ -P (green),<sup>[10]</sup> and red phosphorene;<sup>[11]</sup> nine nonhoneycomb polymorphs  $\varepsilon$ -P,  $\zeta$ -P,  $\eta$ -P,  $\theta$ -P,  $\alpha\varepsilon$ -P,  $\beta\varepsilon$ -P,  $\gamma \epsilon$ -P,  $\delta \epsilon$ -P1, and  $\delta \epsilon$ -P2;<sup>[13]</sup> fibrous like single-layer violet (Hittorf) phosphorus;<sup>[12]</sup> 21 new porous 2D polymorphs through the combination of phosphorus monomer, dimer, trimer, tetramer, and hexamer<sup>[14]</sup>;  $\Psi$ -P;<sup>[15]</sup> Kagome-P;<sup>[16]</sup>  $\alpha$ -P6,  $\beta$ -P6, and 558-P6 containing ridges and having two-, three-, and fourfold coordination,<sup>[17]</sup> and so on. Besides 2D layered phosphorus, novel structures in other dimensions have also been predicted or synthesized, including 0D phosphorus-based fullerenes,<sup>[31]</sup> black-phosphorus quantum dots,<sup>[32]</sup> 1D phosphorus nanotubes,<sup>[31]</sup> as well as 3D covalently linked phosphorus allotropes.<sup>[33]</sup> Partial substitution of phosphorus atoms by another element to form binary phosphides are expected to further tune the properties of phosphorus-based materials. Indeed, some 2D phosphorus compounds have recently been studied theoretically, such as antimony-substituted violet phosphorus (PSb),<sup>[34]</sup> boron-doped  $\alpha$ -phosphorus (BP<sub>3</sub>),<sup>[35]</sup> alloyed arsenic phosphide (AsP),<sup>[36]</sup> germanium-substituted phosphorus (GeP<sub>3</sub>),<sup>[37]</sup> and phosphorus carbide (PC).<sup>[38]</sup> Some of these compounds are even predicted to have properties superior to elemental BP, e.g., the  $\alpha$ -BP<sub>3</sub> bilayer is predicted to have an electron mobility ≈200 times higher than bilayer BP;<sup>[35]</sup> black

 $As_x P_{1-x}$  exhibits tunable bandgap down to the long-wavelength infrared regime.<sup>[39]</sup> The prediction of both the elemental and the binary phosphorus allotropes has greatly enriched the diversity in the 2D phosphorus family. However, research on new 2D phosphorus allotropes is currently unbalanced. The number of theoretically proposed structures far exceeds the experimentally synthesized counterparts. Moreover, even for the most intensively investigated BP, its few-layer form is mainly isolated through mechanical<sup>[6a]</sup> or liquid-phase exfoliation.<sup>[22]</sup> Other approaches, such as plasma thinning,<sup>[40]</sup> chemical intercalation,<sup>[41]</sup> electrochemical exfoliation,<sup>[42]</sup> pulsed laser deposition,<sup>[43]</sup> chemical vapor deposition,<sup>[44]</sup> or high-temperature, high-pressure conversion<sup>[45]</sup> have also been demonstrated. However, these methods are either time consuming, or lack scalability and controllability. To enable mass production of high-quality atomically thin phosphorus layers and to achieve the experimental realization of the theoretically proposed new 2D phosphorene structures, more effort should be paid to the epitaxial growth technique, which has been successfully demonstrated for graphene and other 2D materials, but rarely reported for 2D phosphorene.

## 2.1. Single-Layer Blue Phosphorus on Au(111)

To date, direct epitaxial growth of 2D phosphorene is still a significant challenge. This is on the one hand due to its easy degradation in ambient environment, on the other hand, it is hindered by the limited theoretical understanding of the growth mechanism on different substrates. In this regard, recently, several first-principles calculations were carried out to reveal the critical role of the substrates, the kinetic pathway, as well as the growth intermediates at different coverages. Gao et al. reported that the strong interaction between phosphorus and the substrate can break the phosphorus flakes, while the weak interaction fails to stabilize the 2D flakes.<sup>[25]</sup> A moderate interaction of about 0.35 eV per P atom is preferred for 2D phosphorene growth. Zeng et al. predicted that a GaN(001) substrate is superior for blue phosphorus growth with an intriguing half-layerby-half-layer growth mechanism.<sup>[46]</sup> Han et al. and Oiu et al. both investigated the relative stability of BP and blue phosphorus on metal surfaces, and both studies found that blue phosphorus is the most stable form on metal substrates such as Au(111) and Ag(111), while BP is the most stable phase on metal surfaces such as Al(111), Sn(100).<sup>[47]</sup> These intriguing theoretical findings provide useful guidelines for experimentalists to grow desired phosphorus structures on appropriate substrates.

Experimentally, we realized the growth of single-layer blue phosphorus on Au(111) by molecular beam epitaxy (MBE) in ultrahigh-vacuum conditions.<sup>[48]</sup> Blue phosphorus was first predicted by Zhu et al. based on density functional theory (DFT) calculations.<sup>[8]</sup> It shares the layered structure and stability of BP, with a lower degree of buckling. As shown by the large scale (**Figure 1**a,b) and the atomically resolved scanning tunneling microscopy (STM) images (Figure 1c), a highly ordered hexagonal superstructure is formed by depositing BP precursor onto a heated Au(111) surface (230 °C). Each dark center is surrounded by six white triangles and the distance







**Figure 1.** Single-layer blue phosphorus on Au(111). a) Large scale and b) high-resolution STM images of single-layer blue phosphorus on Au(111). The unit cell is highlighted in (c) with a = b = 14.7 Å. ( $V_{tip} = 0.9$  V, 100 nm × 100 nm;  $V_{tip} = 0.9$  V, 50 nm × 50 nm;  $V_{tip} = 1.0$  V, 8 nm × 8 nm). d) The line profile along the red line in panel (c) reveals a 14.7 Å distance between the dark holes. e) Top view and f) side view of the optimized model for single-layer blue phosphorus on the Au(111) surface. The top (bottom) phosphorus atoms are represented as purple and yellow balls, while the Au atoms are represented as gray balls. g) STM image simulated according to the model displayed in (e). h) Experimentally observed STM image. i) dI/dV curve taken for single-layer blue phosphorus, revealing a bandgap around 1.10 V. Reproduced with permission.<sup>[48]</sup> Copyright 2016, American Chemical Society.

between the dark holes is 14.7 Å (Figure 1d). DFT calculations are performed to obtain an atomic insight of this superstructure and reveals that the surface structure can be explained by a 4  $\times$  4 supercell of blue phosphorus matched with a  $5 \times 5$  supercell of Au(111). Figure 1e,f show the top and side views of the fully relaxed atomic geometries of blue phosphorus on Au(111), where the average height of the top P and bottom P atoms are 3.58 and 2.40 Å, respectively. The different buckling of the top and bottom P atoms leads to the observation of six bright dots in each triangle, and the simulated STM image is in good agreement with the experimental results (Figure 1f-h). Single-layer blue phosphorus is energetically stable on Au(111) with a calculated adhesion energy of 0.27 eV for each P atom. The measured bandgap of 1.10 eV indicates the semiconductor nature of single-layer blue phosphorus. After our work, another experimental study of MBE growth of monolayer blue phosphorus on Au(111) through thermal decomposition of InP was reported.[49]

# 2.2. Quasi-Free-Standing Single-Layer Blue Phosphorus on Tellurium-Monolayer-Functionalized Au(111)

As mentioned, the underlying substrates plays a critical role for the bottom-up growth of 2D phosphorene. It is therefore crucial to search for a suitable substrate to delicately balance the interaction between the phosphorus and substrate for the growth of desired structures. Here, we provide an experimental exploration of the role of substrates by comparing the growth behaviors of phosphorus on Cu(111), Au(111), and

tellurium-functionalized Au(111).<sup>[50]</sup> Phosphorus was found to strongly interact with Cu(111), as revealed by the formation of randomly dispersed phosphorus nanoclusters and single atoms instead of connected flakes (Figure 2a,b), and was further confirmed by the much larger binding-energy shift of the X-ray photoelectron spectroscopy (XPS) peaks of Cu 2p (0.2 eV) and P 2p (0.9 eV) for P/Cu(111) upon phosphorus deposition, compared with the shift of Au 2p (0.05 eV) and P 2p (0.2 eV) for P/Au(111) (Figure 2c-e). Considering the following transfer process of 2D phosphorene for practical applications, it is highly desirable that the initial growth is conducted on a weakly interacting surface. The interfacial interaction between phosphorus and the substrate can be weakened substantially by functionalization of Au(111) with monolayer tellurium (Figure 2f,g), as evidenced by the fixed peak position of Te 3d and Au 4f after phosphorus deposition, as well as the same location of the P 2p peak to that of the bulk BP (Figure 2h-j). DFT calculations can shed more insight on the interaction strength between phosphorus and different substrates. As shown in Figure 2k-m, the calculated binding energy of the 7-P6 cluster on Cu(111), Au(111), and Te/Au(111) are -0.92, -0.63, and -0.11 eV, respectively, while the distance between the edge phosphorus atoms and the three substrates are 2.37, 2.42, and 2.70 Å, respectively. The combination of the STM, XPS, and DFT studies indicate the successful growth of a quasi-free-standing single-layer blue phosphorus on Te/Au(111), which could enable their further application in electronic and optoelectronic devices. In addition to the interfacial interaction, the lattice symmetry also plays a significant role for the phosphorus structure, for example, unlike P/Cu(111), phosphorus nanostripe arrays are formed on Cu(110).<sup>[51]</sup>







**Figure 2.** Growth of quasi-free-standing single-layer blue phosphorus on tellurium-monolayer-functionalized Au(111). a) Large-scale and b) close-up STM image of phosphorus clusters on Cu(111). ( $V_s = 0.5 V$ , 200 nm × 200 nm;  $V_s = 0.5 V$ , 15 nm × 15 nm). c–e) XPS core-level spectra of Au 4f, Cu 2p, and P 2p for clean Au(111), Cu(111), and P grown on these two substrates. f) Atomically resolved STM image of the tellurium layer on Au(111). ( $V_s = 0.7 V$ , 20 nm × 20 nm). g) STM image of single-layer blue phosphorus on tellurium layer. ( $V_s = 1.0 V$ , 50 nm × 50 nm). h–j) XPS core-level spectra of Te 3d, Au 4f, and P 2p for clean Au(111), Te layer on Au(111), and P grown on Te-functionalized Au(111). k–m) Top and side views of seven six-membered phosphorus rings clustered on Cu(111), Au(111), and Te/Au(111). Reproduced with permission.<sup>[50]</sup> Copyright 2017, American Chemical Society.

# 3. Surface Functionalization of BP toward High-Performance Complementary Electronics

Ultrathin BP-configured FET devices generally show ambipolar transport characteristics with strong asymmetry, where the mobility and on-current of the holes are orders of magnitude higher than that of electrons.<sup>[6a,26,52]</sup> This hole-transportdominated behavior seriously limits the applications of BP in complementary electronics, leading to the great necessity to develop effective functionalization schemes to either facilitate the electron transport of BP or dope BP in a controlled and nondestructive manner. Surface charge-transfer doping, based on modifying the surface with a specific adlayer, relies on interfacial charge transfer between the surface dopants and the underlying semiconductors, which does not induce significant defects or destroy the crystal structure of as-doped materials, and is thus known as a nondestructive doping method.<sup>[53]</sup> Compared to the electrostatic modulation via an external electrical field,<sup>[54]</sup> surface transfer doping usually provides a stronger doping capability with the ease of device fabrication. In the pioneering studies, a variety of surface species were utilized to manipulate the electronic and optoelectronic properties of 2D materials (e.g., graphene<sup>[55]</sup> and TMDs<sup>[28,56]</sup>), as well as organic semiconductors.<sup>[53]</sup> In this section, we highlight our recent progress on the surface functionalization of BP via in situ surface charge-transfer doping, with a view toward high-performance

complementary devices.<sup>[19c,57]</sup> Our findings, coupled with the tunable nature of surface functionalization, enable BP as a promising candidate for future complementary electronics.

## 3.1. Cs<sub>2</sub>CO<sub>3</sub>-Functionalized BP

Metal oxides, Cs<sub>2</sub>CO<sub>3</sub> and molybdenum trioxide (MoO<sub>3</sub>), have been widely used in organic electronics<sup>[58]</sup> as well as 2D systems such as graphene<sup>[59]</sup> and TMDs,<sup>[60]</sup> and serve as a strong electron donor and acceptor to modify the doping level of semiconductors, respectively. Recently, we applied surface transfer doping to BP, demonstrating significant electron and hole doping to effectively modulate the ambipolar characteristics of BP, through in situ surface modification with Cs<sub>2</sub>CO<sub>3</sub> and MoO<sub>3</sub>, respectively.<sup>[19c]</sup> Taking Cs<sub>2</sub>CO<sub>3</sub> as an example to illustrate this pioneering work, BP was found to be strongly electron doped by Cs<sub>2</sub>CO<sub>3</sub> overlayers, as revealed by the significant negative shift of the transfer characteristics of BP with the gradual deposition of  $Cs_2CO_3$  in Figure 3a. This n-type doping results in the transition of BP transport properties from holedominated, across balanced ambipolar, and finally to electrondominated behavior, as shown in Figure 3b. More importantly, the electron mobility of BP was remarkably enhanced from 1.1 to 27.1 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> after deposition of 10 nm Cs<sub>2</sub>CO<sub>3</sub> (Figure 3c), indicating a highly improved electron transport in ADVANCED SCIENCE NEWS \_\_\_\_\_





**Figure 3.** BP field-effect transistors functionalized by  $Cs_2CO_3$ . a) Evolution of forward transfer characteristics ( $V_g$  from -80 to 80 V) of a BP FET measured at  $V_{sd} = 0.1$  V in logarithmic scale with increasing  $Cs_2CO_3$  thickness from 0 to 1.5 nm. b) Linear plot of the transfer curves at 0.5 and 10 nm  $Cs_2CO_3$  coverage with respect to the pristine BP. c) Electron concentration ( $n_e$ ) at  $V_g = 30$  V and mobility of BP versus  $Cs_2CO_3$  thickness. d) The plot of BP conductivity at zero gate voltage as a function of  $Cs_2CO_3$  thickness. e) UPS spectra evolution in the low-kinetic-energy region (secondary electron cutoff) with respect to the  $Cs_2CO_3$  thickness. Reproduced with permission.<sup>[19c]</sup> Copyright 2015, Springer Nature.

BP channel. We propose that the n-type doping can significantly increase the electron concentration to fill the electron-trapping sites, as well as to effectively screen the trapped charges in BP, hence greatly enhancing its electron mobility. The underlying interfacial charge transfer between Cs2CO3 and BP was further understood by in situ ultraviolet photoelectron spectroscopy (UPS) measurements on Cs<sub>2</sub>CO<sub>3</sub>-coated bulk BP, as presented in Figure 3e, where the work function of BP sharply decreased from 4.03 eV to 3.1 eV after 1.7 nm Cs<sub>2</sub>CO<sub>3</sub> deposition, originating from the substantial electron transfer from Cs<sub>2</sub>CO<sub>3</sub> to BP. Similar to the case of Cs<sub>2</sub>CO<sub>3</sub>, MoO<sub>3</sub> was also used to hole-dope BP FETs due to its extremely high work function in high vacuum, which shows a giant p-type doping effect on BP devices with nondegraded hole mobility. Moreover, this doping can also tailor the Schottky junctions formed between metal electrodes and BP, and thereby enhance the photoresponsivity of BP-based photodetectors.

#### 3.2. K-Functionalized BP

Since our first investigation of surface transfer doping on BP using  $Cs_2CO_3$  and  $MoO_3$ ,<sup>[19c]</sup> several organic and inorganic species have been employed on BP surface to either modulate its transport properties<sup>[61]</sup> or protect BP from degradation in air.<sup>[29b,62]</sup> Recently, metal adatoms<sup>[61a,b]</sup> and crosslinked poly(methyl methacrylate)<sup>[61c]</sup> were demonstrated to n-type-dope BP for the realization of complementary devices on a single BP flake, such as p–n diodes and logic inverters. However, these electron donors did not create a significant n-type doping effect on BP, thereby limiting the performance of

as-made complementary devices. Herein, we further utilized the alkali metal K, one of the strongest electron donors in nature, to modify the electronic properties of BP, as well as to establish the lateral homojunction on a single BP nanosheet toward high-performance complementary electronics.<sup>[57]</sup>

Similar to Cs<sub>2</sub>CO<sub>3</sub>, K modification exhibits a giant electrondoping effect on BP devices, as suggested in Figure 4a. K doping was found to remarkably enhance the electron mobility of BP by over one order of magnitude to 262 (377)  $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for two-terminal (four-terminal) measurements (Figure 4c), thus approaching the record-high electron mobility of Cudoped BP on BN (380 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) at room temperature.<sup>[61a]</sup> A clear bandgap reduction of BP was also extracted from FET measurements and plotted in Figure 4d, which originates from the Stark effect<sup>[63]</sup> induced by a giant vertical electrical field via K doping. In situ XPS characterizations show a remarkable downward band bending of BP after K doping, in particular by 0.55 eV with a 3.2 nm thick K layer, as illustrated in Figure 4e, confirming the dramatic interfacial electron transfer from K to BP. Furthermore, a spatially controlled K doping technique was developed to establish high-performance complementary devices on a single BP flake. For example, by masking half of the BP channel using lithography technique (Figure 4f), a steep p-n homojunction can be formed between the capped and uncapped BP channels after K deposition, thus achieving an excellent diode performance with a near-unity ideality factor of 1.007 and on/off ratio of  $\approx 10^4$ , as presented in Figure 4h. Based on the realization of both n- and p-type channels in an individual BP flake, a logic inverter device was also constructed via the integration of a K-doped BP FET with a pristine BP FET, giving rise to an inverted output signal with a gain of  $\approx 5$ .







**Figure 4.** K-functionalized BP for high-performance p–n diode devices. a) Evolution of transfer characteristics ( $V_g$  from -80 to 50 V) of a BP FET measured at  $V_{sd} = 0.1$  V in logarithmic scale with increasing K thickness. b) Linear plot of the same transfer characteristics. Inset: schematic illustration of BP devices during the deposition of K. c) The plot of extracted electron concentration at  $V_g = 25$  V and mobility as a function of K thickness. d) Estimated bandgap of the few-layer BP with respect to K thickness. The inset shows the current minimum of the transfer curves as a function of K thickness. e) XPS P 2p core-level spectra of bulk BP as a function of K thickness. f) Schematic illustration and optical image of an as-fabricated p–n diode on a single BP flake. g) The  $I_{sd}$ - $V_{sd}$  characteristics ( $V_{sd}$  from -1 to 1 V) of a 1.6 nm K-coated BP diode in linear scale upon gate voltages ranging from -50 to -10 V with a step of 5 V. Inset: the plot of calculated rectification ratio with respect to K thickness. h) The rectification characteristics of the BP diode at an optimized gate voltage of -30 V in both logarithmic and linear scales. Reproduced with permission.<sup>[57]</sup> Copyright 2017, American Chemical Society.

## 4. Degradation Mechanism of BP

Although BP is the most stable allotrope of phosphorus, fewlayer BP suffers from poor air stability and can be easily oxidized in air, thus seriously degrading its device performance. To develop effective protection schemes to achieve air-stable BP devices, it is crucial to understand the underlying oxidation mechanism of BP in air ambient. Gomez et al. attributed the degradation of BP to its intrinsic hydrophilic surface and long-time exposure to air.<sup>[64]</sup> Pioneering theoretical work by Zettie et al. proposed oxygen as the main reason for BP degradation and proposed a triplet-to-singlet conversion of oxygen molecules that largely lowers the oxygen dissociation barrier and thus enhances the oxidation possibility.<sup>[65]</sup> In general, light illumination can serve as the excitation source to trigger the chemical reaction between BP and adsorbed oxygen. This lightinduced oxidation mechanism was first proposed by Favron et al.<sup>[66]</sup> and further supported by Walia et al.<sup>[67]</sup> by using in situ Raman spectroscopy characterization. They hypothesized that oxygen, water, and visible light are simultaneously required for BP degradation. Subsequently, theoretical work by Zhou et al. proposed a three-step oxidation route of BP including the generation of superoxide upon light illumination, dissociation of the superoxide, and breakdown of BP lattice assisted by water.<sup>[30b]</sup> However, to date, how the air components (e.g., O<sub>2</sub> and H<sub>2</sub>O) interact with the BP surface and impact on its device performance are still not well understood. For example, it is still controversial whether light illumination is necessary for BP oxidation in air, and the exact role of water during the oxidation process is still unclear. In this section, we highlight our recent advances on exploring the role of O<sub>2</sub> and H<sub>2</sub>O in oxidizing BP, as well as tuning its electronic properties, via well-controlled in situ characterizations under different environments.<sup>[68]</sup> Our findings pave the way for the development of

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proper protecting schemes toward BP-based high-performance electronic devices.

#### 4.1. Physisorption of Oxygen and Light-Induced Oxidation

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Although the light-induced oxidation mechanism was previously proposed, the interaction between BP and pure oxygen has not been well understood. Recently, we clearly demonstrated the physisorption of oxygen on the surface of BP in the absence of water and light, which leads to a significant modulation of the BP's transport characteristics.<sup>[68a]</sup> The exposure to oxygen dramatically attenuated the electron transport of the BP, showing a decrease of electron mobility of the BP by over three orders of magnitude, while the hole mobility was nearly retained, as indicated by Figure 5a,b. The transport behavior was nearly reversible to the pristine state after annealing (Figure 5b), suggesting that O<sub>2</sub> molecules were physically adsorbed on the BP surface. This physisorption nature was further revealed by in situ XPS measurements (Figure 5b), where the phosphorus oxide (PO<sub>x</sub>) peak ( $\approx 134-135$  eV)<sup>[30a]</sup> did not appear in the P 2p core-level spectra during O<sub>2</sub> exposure (Figure 5b). DFT calculations have revealed that the unoccupied states of physisorbed O<sub>2</sub> on BP serve as an electron-trapping source in the BP channels. On the other hand, O<sub>2</sub> exposure under light illumination clearly triggers the oxidation of BP, hence irreversibly degrading the device performance by seriously suppressing both electron and hole transport in BP FETs, as shown in Figure 5d,e. In situ XPS characterization has confirmed the chemisorption of oxygen on BP under light illumination, as revealed by Figure 5f, which exhibits an obvious  $PO_x$ peak located at the binding energy of ≈134.5 eV with increasing exposure time. Our results further clarified the light-induced oxidation of BP without the impact of water, which demonstrates

the formation of intermediate superoxide anions  $O_2^-$  by trapping the photogenerated electrons in the BP, thus leading to the BP oxidation.

#### 4.2. Water-Catalyzed Oxidation

Since the proposal of light-induced oxidation, it has been generally accepted that light is the prerequisite to initiate BP oxidation in air,<sup>[30c]</sup> while the impact of water molecules on degrading BP has not been fully understood. We recently demonstrated a new degradation channel of BP through water-catalyzed oxidation in a dark environment.<sup>[68b]</sup> It was found that exposure to humid oxygen can significantly degrade the device performance of BP FETs even without light irradiation, presenting over two orders of magnitude mobility decrease for both electron and hole transport, as illustrated in Figure 6a,b. The oxidation of BP was further verified by XPS results that show a PO<sub>x</sub> peak in the P 2p core-level spectra (Figure 6c), similar to our previous work.<sup>[68a]</sup> By contrast, humid nitrogen exposure neither created phosphorus oxides on BP nor deteriorated its transport properties, suggesting the nonoxidative nature between BP and water molecules. Having established the physisorption of O2 on BP without  $H_2O$  (Figure 5a–c), we attributed the oxidation of BP in dark environment to the coexistence of O<sub>2</sub> and H<sub>2</sub>O, i.e., water can catalyze the chemisorption of O<sub>2</sub> on the surface of BP.

Detailed DFT calculations have revealed the underlying mechanism of this water-catalyzed oxidation. Due to the strong polarization of H<sub>2</sub>O molecules, the energy levels of the degenerated  $\pi^*_{2p}$  orbitals of O<sub>2</sub> ( ${}^{3}\Sigma_{g}^{-}$ ) were found to be largely lowered by approaching H<sub>2</sub>O to O<sub>2</sub>, as shown in Figure 6d, thus resulting in significantly enhanced electron affinities (i.e., electron-accepting ability) of O<sub>2</sub>. The calculated band structures of BP-O<sub>2</sub> and BP-O<sub>2</sub> · H<sub>2</sub>O systems (Figure 6e) further illustrate



**Figure 5.** a-f) FET and XPS characterizations on BP with the exposure to pure oxygen a-c) without and d-f) with light illumination. a,d) Linear plots of the transfer characteristics upon 1280 min exposure with respect to the pristine BP. b,e) Logarithmic plots of the transfer curves after annealing compared to pristine and 1280 min exposed curves. c,f) P 2p core-level XPS spectra evolution of BP as a function of exposure time. A 515 nm laser with the intensity of  $\approx 1.5$  W cm<sup>-2</sup> was used for light illumination. Reproduced with permission.<sup>[68a]</sup> Copyright 2017, IOP Publishing Ltd.







**Figure 6.** The effect of humid oxygen exposure on BP. a) Evolution of transfer characteristics (at  $V_{sd} = 0.1$  V) of a BP FET device on a linear scale for different humid O<sub>2</sub> exposure times. Inset: The plot of the transfer curve on a logarithmic scale after 19.5 h exposure with respect to the pristine curve. b) Extracted electron and hole mobility versus exposure time. The inset is the schematic plot of the humid O<sub>2</sub> exposed device. c) The evolution of P 2p core-level XPS spectra after the exposure to humid O<sub>2</sub>. d) Electron affinities, relative energies of O<sub>2</sub>–H<sub>2</sub>O clusters, and energy levels of  $\pi^*_{2p}$ , orbitals of O<sub>2</sub> as a function of the distance (*d*) between O<sub>2</sub> and H<sub>2</sub>O. Electron affinities are in red, relative energies are in blue, and orbital energies are in black, units are in eV. e) Band structures of BP–O<sub>2</sub>, BP–O<sub>2</sub>·H<sub>2</sub>O, and BP–O<sub>2</sub>·2H<sub>2</sub>O systems; the flat bands appear in the bandgap of BP, which are contributed from O<sub>2</sub> in all cases. f) Charge-density difference between BP–O<sub>2</sub> and BP–O<sub>2</sub>·H<sub>2</sub>O, and BP–O<sub>2</sub> and BP–O<sub>2</sub>·2H<sub>2</sub>O. The yellow and cyan volumes represent electron accumulation and depletion, respectively. The isosurface corresponds to 3.4 × 10<sup>-3</sup> e Å<sup>-3</sup>. Reproduced with permission.<sup>[68b]</sup> Copyright 2017, Wiley-VCH.

the decrease of the O<sub>2</sub> energy levels with respect to the BP band structure under the action of H<sub>2</sub>O. This facilitates electron transfer from BP to O<sub>2</sub> (Figure 6f) to form the O<sub>2</sub><sup>-</sup>·H<sub>2</sub>O cluster with lower energy barrier to oxidize BP,<sup>[30b]</sup> thereby accelerating the oxidation process. Finally, the hydrogen bond of water molecules continues pulling the formed P–O bond on the BP surface to further deteriorate the BP lattice, as well as degrade the BP to phosphorus acid (e.g., H<sub>3</sub>PO<sub>4</sub>),<sup>[30b]</sup> which enables the exposure of the BP beneath to O<sub>2</sub> and continuous oxidation of BP.

## 5. Conclusion and Perspectives

Here, we have reviewed our recent progress on the exploration of epitaxial growth, surface functionalization, and degradation mechanism of 2D phosphorene. The epitaxial growth of 2D phosphorene on metal substrates with different interactions is systematically demonstrated, which provides two guidelines for the future selection of substrates. First, the substrate should have relatively weak interactions with the phosphorus; second, substrates with appropriate symmetry and matched lattice constant are preferred. In addition, surface functionalization of BP via surface transfer doping with  $Cs_2CO_3$  and K are demonstrated to achieve high-performance complementary devices. Finally, we have highlighted the effect of oxygen in the presence of light or water on degrading BP, thus providing a comprehensive understanding of the oxidation process of BP in air ambient.

Current research on 2D phosphorene is still in the early stage of development, and many fascinating new directions need to be explored in the near future. One of the most important technological breakthrough needed is the bottom-up growth of large-scale and high-quality single/few-layer 2D phosphorene sheets. The combination of experimental and theoretical studies is necessary to provide useful guidelines, where theoretical calculations can help to evaluate the interaction between the phosphorus and the substrate and unveil the growth dynamics, thus preventing unnecessary trials on unsuitable substrates. In addition, part of ongoing research effort will be devoted to the direct growth of 2D phosphorene-based vertical heterojunctions. Recently, van der Waals heterostructures, which are vertically stacked layer by layer by multiple 2D materials, have created a new platform in materials science for exploring new physics and developing devices with novel architectures or functionalities. Hybridization of phosphorene with other 2D members could provide opportunities for the realization of novel electronic and optoelectronic devices, e.g., stacking the p-type phosphorene on n-type TMDs to construct vertical p-n junctions, inserting BP between two graphene layers to investigate the tunneling behavior, or studying the photogeneration process on phosphorene-based heterostructures, etc. Furthermore, point defects in crystal lattice such as vacancies, adatoms, antisites, and dopant atoms can be used to tailor the electronic, optical, magnetic and catalytic properties of 2D materials. Controllable and scalable sample growth with application-oriented defect engineering will be another intriguing direction and hopefully enable new breakthroughs with 2D phosphorene. Going



beyond defect engineering, continuous efforts on searching for more efficient surface functionalization approaches to effectively tune the fundamental properties of phosphorene are still needed to achieve high-performance multifunctional devices. An ideal functionalization layer could enhance the device performance and meanwhile protect and stabilize phosphorenebased devices for long-term applications. Last but not least, the chemical instability of 2D phosphorene remains a critical bottleneck that limits its practical applications, and needs to be seriously addressed in future phosphorene-based electronics.

## Acknowledgements

J.L.Z., C.H., and Z.H. contributed equally to this work. The authors acknowledge financial support from NSFC grant under Grant No. 21573156, Natural Science Foundation of Jiangsu Province under Grant No. BK20170005, National Science Fund for Distinguished Young Scholars of China (Grant No. 61525404), Singapore MOE Grant (Grant No. R143-000-652-112), Fundamental Research Foundation of Shenzhen (Grant No. JCYJ20170817100405375), Shenzhen Peacock Plan (Grant No. KQTD2016053112042971), and Science and Technology Planning Project of Guangdong Province (Grant 2016B050501005).

# **Conflict of Interest**

The authors declare no conflict of interest.

# **Keywords**

2D phosphorene, electronic devices, epitaxial growth, interface engineering

Received: April 6, 2018 Revised: May 17, 2018 Published online:

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