A Ray of Hope for Future Technology: Phosphorene

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Abstract

In the recent times, two dimensional layered single crystals attracted huge attention to their tunable mechanical, optical and electronic properties which have potential applications in future nanoelectronics and optoelectronics for large scale integration in low power technology. Phosphorene, the single- or few layer form of black phosphorus, was lately investigated as a two dimension layered material with motivating promising applications in the field of nanoelectronics and optoelectronics. However, there is still a need for developing its fundamental properties, design schemes and growth techniques. In this context, we review about the recent progress in phosphorene studies, primarily on the fabrication process, properties, forthcoming applications and challenges. In this article, the anisotropic properties (electronic, optoelectronic, thermoelectric and mechanical) of phosphorene, due to its puckered structure is also highlighted. The extraordinary properties of phosphorene make it a future material for designing and fabrication of nanodevices, and more fundamental and technological developments can be established in the near future.

Keywords: 2D Layered Materials, Black Phosphorus (BP), Electronics, Optoelectronics, Phosphorene

1. Introduction

Phosphorene, a semiconducting material, is a two-dimensional material and allotrope of phosphorus. Among phosphorus allotropes, Black Phosphorus (BP) has been recognized as the most stable2,2D layered material having a puckered structure as well as weak van der Waals interlayer (vdWs) interaction1. Phosphorene can be viewed as a mono layer or multilayer of (BP), much in the same way as graphene is a single layer of graphite4. It is the only elemental 2D material, apart from graphene, that is capable of supporting electronic devices due to its high carrier mobility2 and an effective band gap3.

Due to great demands for high-performance devices, great deal of attempts has been made towards discovering of additional layered materials that exhibit an expended operating range in their fundamental properties such as electronic band gap and carrier mobility2,2D. Graphene is the first material discovered which had shown significant promises for its high conductivity10 and carrier mobility at room temperature11. But the material lacks a natural band gap12 that could be used to switch this flow on and off. This reduces graphene’s usefulness as a replacement for the semiconductor switches in computer circuits13. Recently, phosphorene has been attracted researcher’s interest due to its unique properties and great potentials in the field.
of nanoelectronics and optoelectronics for large scale integration in low power technology\cite{13,14}. Phosphorene is also highly promotable for optical applications\cite{16}, due to its intrinsic semiconducting nature and presence of direct band gap. Due to its band gap, it can be switched between insulating and conducting states, and is still flat enough to confine electrons so that charge flows quickly, leading to a relatively high mobility\cite{20}.

Although, phosphorene seems more stable than its competitors such as graphene, silicene and germanene\cite{21}, but it is not easy to fabricate and phosphorene’s success in electronics will depend on whether researchers can find efficient ways to extract single layers and deposit them on substrate.

\section*{2. Structure}

Among phosphorus allotropes\cite{1,2}, BP has been recognized as the most stable 2D layered material having a puckered structure as well as weak van der Waals (vdWs) interlayer interactions\cite{3}. The initial structures of monolayer and few-layer phosphorene were obtained from bulk BP\cite{22,23}. Monolayer black phosphorus has a puckered honeycomb structure with each phosphorus atom covalently bonded

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{structure.png}
\caption{(a) Three dimensional structure of phosphorene\cite{22} (b) crystal structure of black phosphorus\cite{3} (c) top view of single layer phosphorene (d) P-P bonding configuration\cite{24}.}
\end{figure}
with three adjacent atoms. For illustration, Figure 1 displays the 3D view of phosphorene structure\textsuperscript{22}.

The crystal structure of BP is shown in Figure 1. At ambient conditions, BP crystallizes in a base-centered orthorhombic structure\textsuperscript{2}. The lattice parameters\textsuperscript{1} are \(a = 3.3133\), \(b = 10.473\), and \(c = 4.374\) Å. Phosphorene differentiates itself from other 2D layered materials by its exclusive structural characteristics. Along the armchair direction, it has a puckered structure but along the zigzag direction, it turns out as a bilayer configuration (Figure 1). This anisotropy in structure can be surely seen in its local bonding configurations. The crystal structure of black phosphorous consists of puckered layers of P atoms with three short covalent bonds. The value of bond angle, along the zigzag direction is found to be 96.3° and is known as the hinge angle. The calculated adjacent P-P bond length is 2.224 Å. Both these values are smaller than the corresponding dihedral angle (102.95°) and the connecting bond length (2.244 Å) along the zigzag direction (Figure 1)\textsuperscript{34}. According to the stacking pattern, BP’s interlayer distance varies between 3.21 and 3.73 Å\textsuperscript{3-15}. The orthorhombic unit cell consists of eight phosphorus atoms which gives a calculated density of 2.69 g cm\(^{-3}\). The nearest (\(d_1\)) and next-nearest (\(d_2\)) atomic separations (in Figure 1(b)) between the layers are 3.6 and 3.8 Å\textsuperscript{15}.

The crystal structure of black phosphorus can be highly segregated under high pressure. This usually comes from the anisotropic compressibility of black phosphorus, due to the asymmetrical crystal structures\textsuperscript{20-23}. Such a rare structural arrangement which resembles to a network of connected hinges (see Figure 1), is the origin of the anisotropic physical\textsuperscript{36-39} and mechanical properties\textsuperscript{38-41}, and it has given rise to specific nano-device designs utilizing this directional selectivity\textsuperscript{35-37}.

### 3. Properties of Phosphorene

Due to the unique puckered honeycomb structure, phosphorene shows anisotropic natures of electronic and phonon dispersions, which results in anisotropic electric-transport, thermal transport and optical properties. Moreover, the puckered honeycomb structure leads to characteristic mechanical properties, especially significant flexibility against tensile and compressive strains. This section introduces the ongoing status on the understanding of physical and mechanical properties of phosphorene with an emphasis on its unique peculiar anisotropy in structure and property.

#### 3.1 Electronic Property

Multilayer phosphorene films have been recognized as a novel p-type 2D semiconductor\textsuperscript{12} with unique electrical properties as well as great carrier mobility. Recent theoretical studies have predicted that monolayer black phosphorus can have an extremely high hole mobility\textsuperscript{2,17,38}. Researchers found out that carrier mobility rises by factor of 5 when phosphorene temperature decreases from room temperature to 10 K\textsuperscript{24}. In recent times, researchers concluded that FETs produced by few-layer BP had exceptional electronic properties and a high on-off ratio of 10\(^6\) with a carrier mobility of 1000 cm\(^2\)V\(^{-1}\)S\(^{-1}\)\textsuperscript{16}.

Depending on the thickness (number of layers), multi-layer phosphorene has classified in the strong band-gap semiconductors with a direct band gap of 0.3 eV which is determined by first principle calculations\textsuperscript{11} and angle-resolved photoemission spectroscopy\textsuperscript{12,43}. As the thickness decreases, the band gap constantly increases due to quantum confinement, reaching 2 eV for monolayer phosphorus\textsuperscript{33}. The moderate band gap of black phosphorus (~0.3eV) in its thin film form can bridge the energy gap between the zero bandgap of graphene\textsuperscript{12} and the relatively large band gap of many transition metal dichalcogenides (1.5-2.5eV)\textsuperscript{34}. Besides, the thickness of black phosphorus, strain is predicted to be an effective way for tuning the band gap\textsuperscript{34}. It has also been reported that a uniaxial compressive or tensile strain can switch black phosphorus from nearly a direct band gap semiconductor to an indirect band gap semiconductor, semi metal or metal\textsuperscript{34}. As a result, single-layer to thin film black phosphorus can cover a broad energy spectrum and interact strongly with electromagnetic waves in the mid-infrared, near-infrared, and visible frequency range where many important applications in defense, medicine and communication lie, such as night vision, thermal imaging and optical communication networks\textsuperscript{13}.  

3.2 Transport Properties

The transport properties of few layer BP lie between that of graphene and most TMDs (such as MoS$_2$ and WSe$_2$). Such properties of black phosphorus may be attractive for building gigahertz frequency thin film electronics. Various groups have measured the Hall mobility of BP sample of various thicknesses and at different temperature ranges. The Hall mobility of an 8-nm-thick black phosphorus sample, along a randomly chosen direction, has been calculated around 210 cm$^2$.V$^{-1}$.s$^{-1}$ at room temperature. Also, at higher temperature, its value is found to be around 350 cm$^2$.V$^{-1}$.s$^{-1}$ for the same sample. The Hall mobility of a 15 nm thick black phosphorus thin film, along the light effective mass (x) direction is measured around 600 cm$^2$.V$^{-1}$.s$^{-1}$ at room temperature and above. Below 120 K, its calculated value is 1,000 cm$^2$.V$^{-1}$.s$^{-1}$. The Hall mobility of holes goes beyond 1,000 cm$^2$.V$^{-1}$.s$^{-1}$ at 300 K and 55,000 cm$^2$.V$^{-1}$.s$^{-1}$ at 30 K, respectively, along the x direction in bulk BP. The electron mobility along the x direction is also estimated near to 1,000 cm$^2$.V$^{-1}$.s$^{-1}$ at 300K and is above 10,000 cm$^2$.V$^{-1}$.s$^{-1}$ at 50K. These aspects are crucial for making transistors with high current and power gains that are the most significant features for designing high-frequency power amplifiers and high-speed logic circuits. In addition, transistors based on black film showed excellent current saturation and on-off current ratio above $10^5$, both offering key advantages over graphene transistors for analog and digital electronics.

The resistivity of BP was first calculated by Bridgman, approximately ranges between 0.48 and 0.77 Ω-cm at 30°C, and to be about 35% less at 75°C. The temperature dependence of resistance displays the behavior characteristic to the small band gap semiconductors in which both holes and electrons contribute to transport at high temperature. Later on, it was revisited that undoped samples of BP shows p-type conductivity with the positive value of Hall coefficient. This showed that conductivity is more controlled by holes instead of the electrons. The dependence of conductivity on temperature proclaimed an energy gap of around 0.33 to 0.35 eV. Although the interlayer conductivity is much smaller than the in-plane conductivity reflecting the layered structure, the interlayer coupling is not negligible at the ambient pressure.

3.3 Thermoelectric Performance

Phosphorene exhibits promising future for thermoelectric applications. Theoretically, performance of thermoelectric devices depends upon the Seebeck effect in order to convert heat energy to electricity. The ratio of a device’s electrical conductance to its thermal conductance is known as Seebeck coefficient. The desirable alignment of phosphorene with high electrical conductivity and poor thermal conductivity has remarkably boosted its thermoelectric performance accordingly. This is due to the notable electron transport in phosphorene which takes place along its armchair direction, and causes poor thermal conductance.

The thermal conductivity of phosphorene is apparently predicted to be much smaller than that of graphene and TMDs. Apart from that, it is also recorded that the thermal conductivity of phosphorene is vastly anisotropic. It is expected that the value of thermal conductivity along zigzag direction is much larger than that along the armchair direction. Such anisotropic behavior of the thermal conductivity is originated from the anisotropic phonon dispersion due to its puckered structure. From theoretical analysis, it is indicated that the sound velocity along zigzag direction is about twice larger than that along armchair direction, which leads to the anisotropic thermal conductivity.

It is also investigated that thermal conductivity can be modulated by strain effect which indicates that in the case of applying biaxial strain and uniaxial strain parallel to armchair direction, the thermal conductivity of both zigzag and armchair direction is reduced. However, in the case of applying uniaxial strain parallel to zigzag direction, the thermal conductivity parallel to zigzag direction is enhanced while armchair direction is decreased. Such anisotropic strain dependence of the thermal conductivity is due to the enhancement of the contribution of the low frequency phonon modes. These theoretical results indicate the possibility to modulate the thermal conductivity of phosphorene by strain.
In the theoretical study, it is suggested that phosphorene is a promising thermoelectric material. The electrical conductivity and thermal conductivity show in-plane anisotropy and the preferred direction of electrical conductivity and thermal conductivity is orthogonal to each other. The preferred direction of electrical conductivity is parallel to armchair direction, although that of thermal conductivity is parallel to zigzag direction. Such orthogonal relation can lead to the enhancement of the efficiency of the thermoelectric conversion.

3.4 Mechanical Properties

The mechanical properties of 2D monolayer phosphorene and few-layer black phosphorus through first principles DFT, have been calculated and results show the highly anisotropic and nonlinear mechanical properties due to its unique puckered structure. Monolayer phosphorene can withstand stress up to 18 GPa and 8 GPa in the zigzag and armchair directions, respectively. A monolayer or single layer phosphorene can afford tensile strains up to 27% in zigzag direction and 30% in the armchair direction, while few-layer BP can bear strain up to 32%. However, there is a noticeable difference in the deformation modes under various strain conditions. This strain limit of phosphorene is due to its rare puckered crystal structure. It is observed that the tensile strain applied in the zigzag direction produces a larger P-P bond prolongation, while in armchair direction; the applied tensile strain extends the pucker of phosphorene without stretching the P-P bond lengths.

Such characteristics lead to a direction-dependent Young’s modulus. The two-dimensional effective Young’s modulus of single-layer BP is 166 GPa and 44 GPa along the zigzag and armchair direction, respectively and the average value of Young’s modulus among all the directions is found to be 94 GPa [see Figure 2]. These values of Young’s modulus for phosphorene are much smaller than the effective Young’s modulus of the single-layer MoS2, which is above 270GPa. The values are also one order of magnitude smaller than the effective Young’s modulus in single-layer graphene, which is around 1TPa. The much smaller Young’s modulus of phosphorene, compared to other 2D materials, suggests great applications in strain engineering.

Phosphorene also shows direction dependent Poisson’s ratio, and its value (0.62 to 0.73) along the zigzag direction is 2-4 times larger (0.17 or 0.4) than that in the armchair direction (see Figure 2(b)). This behavior

![Figure 2](image.png)

**Figure 2.** (a) Direction dependence of Young’s modulus of single-layer BP (b) direction dependence of Poisson’s ratio of phosphorene.
of single-layer BP is intrinsic, and arises from its puckered structure, where the pucker can be observed as a re-entrant structure which is composed of two coupled orthogonal hinges. Due to this kind of atomic structure, the value of Poisson’s ratio is observed negative in out-of-plane direction under uniaxial deformation in parallel direction to the pucker.

3.5 Optical Properties

Interlayer coupling plays a critical role in layered materials and it can be directly reflected by low-frequency breathing modes and shear modes of Raman spectra. For example, with different thicknesses, anisotropic effect of the interlayer coupling has been demonstrated because of a strong orientation-dependence of the lattice constant. Moreover, as the thickness increases, large interlayer force constant originating from the sizable covalent interaction between phosphorus atoms in adjacent layers has been confirmed, because the breathing modes have a large red shift in frequency.

Reflecting the anisotropic band structures, optical absorption spectra show linear dichroism for incident light along the \( z \)-direction and linearly polarized in the armchair \( (x) \) and zigzag \( (y) \) directions. For a dielectric polarization in the \( x \)-direction, the peak is found at 1.55 eV in monolayer phosphorene, and with increasing layer number; it monotonically reduces, and reaches to 0.46 eV in bulk BP. For \( y \)-polarized light, on the other hand, only a slight decrease is found from 3.14 eV in monolayer to 2.76 eV in bulk BP with increasing layer number. Another result is that, from the infrared (IR) to visible light range, BP strongly absorbs the light polarized along the \( x \)-direction, but it is transparent to the light polarized along the \( y \)-direction. This is because the dipole operator connects the valence band and conduction band states for the \( x \)-polarization, but symmetrically forbidden for the \( y \)-polarization.

Such an anisotropic optical absorption can be utilized to determine the crystal axis. The optical properties (IR and Raman) enable us to instantly determine the crystal orientation or layer number without a help of Transmission Electron Microscope (TEM) or scanning tunneling microscope.

3.6 Superconductivity

Phosphorene has also been expected to become superconducting near transition temperatures 4.7 K at the simple cubic phase. Depending on temperature and pressure, following three paths were examined, to observe the superconductivity in phosphorene. (1) First, at room temperature, high pressure near about 15 GPa was applied to convert the sample into simple cubic phase, and then the temperature of pressure cell was decreased to liquid helium temperature. In this condition, the critical temperature was measured to be around 6 K and increased insignificantly with increasing pressure. (2) In second process, samples were transformed into the rhombohedral phase by applying approx. 8.7 GPa pressure at room temperature and then the pressure cell was cooled down to liquid helium temperature. Now, the pressure dependent critical temperature was measured. Transition noticed at 8.7 GPa recommended the possibility of superconductivity in the rhombohedral phase. (3) In third process, samples were first cooled down to liquid helium temperature at normal pressure and then critical temperature was calculated by applying high pressures. The value of critical temperature upturned from 4 K to 10.7 K when pressure was increased from 11 to 30 GPa. Moreover, the transition temperature was decreased promptly by decreasing the applied pressure and became null before around 3 GPa in comparison to the first path.

To explain the superconductivity in BP, two mechanisms were applied. One is related with dislocations existing in BP crystals. Atoms are comparatively more mobile near the dislocations. Therefore, phase transition from orthorhombic to simple cubic through the rhombohedral phase would appear around dislocations even at low temperature.

So, this might be a reason that black phosphorus is converted to semiconducting phase matrix with metallic fine threads as a mixed system. The exhibition of superconductivity might be possible in such type of systems. Second, as mentioned above, the energy gap is related to applied pressure. The band gap disappears at about 1.7 GPa with a metallic state transition without changing the structure. The superconductivity examined in the third path of BP is different, which shows that the material...
property of BP can be significantly changed under high pressure as shown in Figure 3.

4. Fabrication Process

Although phosphorene has attracted much attention in electronics and optoelectronics as a new type of two-dimensional material, in-depth investigations and applications have been limited by the current synthesis techniques. Current methods employed to achieve thin pieces of BP are identical to those proven to work with graphene\textsuperscript{69–79}. The first is by top-down processes based on large-scale exfoliation of the bulk material precursor, for example through mechanical exfoliation with tap, liquid exfoliation method\textsuperscript{80–82}, lithiation process\textsuperscript{83–85} and second is by bottom-up large scale growth of 2D materials, for example using chemical vapor deposition processes\textsuperscript{86–92}.

Generally, layered BP or phosphorene has been isolated in the laboratory through mechanical exfoliation with tape and liquid exfoliation methods, from bulk BP. However, out of the limiting factors for the applications of 2D BP is that current methods cannot achieve large area few/single layer phosphorene. Also, this method of production of phosphorene is limited to laboratory usage only. Therefore, advanced mass production techniques are extremely required for industrial applications. However, an intensive research has been carried out for the growth of large area 2D BP by the chemical deposition method.

The unique properties (such as optical, electrical, electronic, thermal, mechanical etc.) of phosphorene have attracted researcher’s attention. So, for utilizing the superior properties of phosphorene into high performance device applications, it is very essential to produce the atomically thin, layered phosphorene with uniform size.

4.1 Mechanical Exfoliation Method

The segregation of single-layer graphene by mechanical exfoliation method, in which bulk layered materials down to the single and few-layers, has opened a new area of research toward investigation of 2D materials properties and applications\textsuperscript{90–94}. One of the essential requirements in

Figure 3. Phase diagram of black phosphorous\textsuperscript{50}.
this method is that the interlayer interaction in layered materials is restrained by weak vdW forces, making possible the cleavage of the materials using just an adhesive tape or scotch tape. Scotch-tape based micro-cleavage of the layered BP and MoS$_2$ crystals is used for fabrication of all 2D devices containing phosphorene or MoS$_2$ layers, followed by shift onto the Si/SiO$_2$ substrate. Then, all samples were successively cleaned to remove any scotch tape residue by using acetone, isopropyl alcohol and methanol. After that, at high temperature around 180$^\circ$C, post bake process is used to eliminate the solvent residue.

High purity and flawless single-crystal flakes are produced by mechanical cleavage method, that are appropriate for fundamental characterization and for fabrication of devices. However, only a small amount of single layer nanosheet materials can be fabricated by this method. Another problem is lack of precise control of flakes size and thickness. Since thickness is one of the critical parameters that defines the electronic, optical and thermal properties of two-dimensional crystals, it is natural to ask for monolayer phosphorene. For this purpose, some other improved fabrication techniques have also been proposed recently. Lu and colleagues demonstrated first successful experimental approach to fabricate monolayer phosphorene by mechanical cleavage and the following Ar$^+$ plasma thinning process. This method serves a better way for controlling thickness and uniformity of monolayer and few-layer phosphorene, but still this technique is not capable for mass production and scale-up applications due to the requirement of laser raster scanning.

4.2 Liquid Exfoliation Method

Modified mechanical exfoliation is one of the synthesis route of phosphorene in which silicon-based transfer layer is utilized to increase the yield of BP flakes, but it is not proper for mass production.

Liquid exfoliation techniques are very promising to produce high yield and sizes of exfoliated phosphorene nanosheets. The interlayer intercalation, often of ionic species, increases the interlayer distance and weakens the interlayer bond to allow the exfoliation of layers in liquid. A number of successful syntheses of 2D materials using liquid exfoliation have been reported by Coleman and co-workers including transition metal dichalcogenides (MoS$_2$, WS$_2$, MoSe$_2$ etc), hexagonal boron nitride (h-BN), and bismuth telluride (Bi$_2$Te$_3$) as well as graphene. Therefore, liquid phase preparation approaches can be effectively employed to produce exfoliated phosphorene nanosheets also in greater quantities. In this method, a layer of bulk black phosphorus is immersed into, typically $N$-methyl-2-pyrrolidone (NMP) solution which is further sonicated to conduct liquid exfoliation. The solution is then centrifuged to remove any unexfoliated BP and to separate thick layers of phosphorene (5–12 layers) from NMP. This method produces macroscopic (milligram-to-gram scale) quantities of monolayer and few-layer phosphorene with excellent water stability, controllable size and layer number, as well as in high yield. Further, efforts are made to optimize the process parameters for producing pristine single layer phosphorene nanosheets of significant size. The scalable nature of the process is important to future electronics industries based on two-dimensional direct band gap semiconductor devices.

Recently, it is found that for the fabrication of uniform and atomically thin phosphorene nanoflakes, aprotic and polar solvents (dimethylformamide (DMF) and dimethyl sulfoxide (DMSO)) are most appropriate. The prepared samples were sonicated and then centrifuged to separate thinner layers of phosphorene (1–7 layers). The synthesized phosphorene nanoflakes demonstrated competitive electrical properties comparing with BP produced via mechanical exfoliation. This method introduces new possibilities for mass production of BP nanolayers to be extensively used in optoelectronics and electronics devices.

4.3 Lithiation or Intercalation Method

Another promising method is lithium intercalation or lithiation process which is faster and more controllable method to produce phosphorene. In this method, lithium foil is used as anode and a layered bulk material-coated Cu is used as the cathode in an electrochemical cell. The resulting Lithium intercalated material is then sonicated in water or ethanol and produce well-dispersed two dimensional nanosheets. Recent calculations show...
that the structure of phosphorene is not much affected by lithiation and the volume change is only 0.2%. The interlayer intercalation will weaken the interlayer bond and allow exfoliation followed by ultrasonication as seen in graphene and TMDC materials.\(^1\)

### 4.4 Chemical Vapor Deposition Method

The advancement of wafer-scale fabrication techniques, through chemical vapor deposition on metallic substrate and epitaxial growth on insulating substrate has made possible large-scale device synthesis based on 2D materials such as graphene and TMDCs. Chemical vapor deposition method is a bottom-up approach to grow 2D layered materials. Current methods employed to achieve thin pieces of BP are identical to those proven to work with graphene. A method is demonstrated towards large-area (up to 4 mm) synthesis of a BP thin film with a thickness of around 40 nm, on flexible substrates. In this method a thin RP film is first deposited onto the substrate by using thermal deposition, which is subsequently converted into a BP film by pressurization in an anvil cell. The conversion process is carried out at room temperature and at a pressure beyond 8 GPa for complete conversion from Red Phosphorus to Black Phosphorus.

Recently, a new method is demonstrated to growing substrate black phosphorus (SBP) directly on a silicon substrate beginning with a thin film of red phosphorus. When substrate containing the amorphous red phosphorus thin films were heated in the presence of Sn/SnI\(_4\) (10 mg) mineralizing agents in argon at high pressure (27.2 atm), SBP of various thickness were found to grow directly on the silicon substrate with continuous regions as large as 9000 \(\mu\)m\(^2\) and roughly 600 nm thick, however, thinner samples were observed throughout the substrate with thickness down to 3.4 nm. This process eliminates the problems associated with the sealed ampoule growth, such as difficulties in sealing the ampoule and potential combustion and also eliminates use of expensive anvil cells. Optimization of the pressure and temperature ramp is currently ongoing aiming at the growth of super large area BP films with few-layer BP sheets for a variety of practical applications in the fields of nanoelectronics and optoelectronics. Therefore, efficacious experimental techniques to produce phosphorene nanosheets are playing an essential role in device applications.

In contrast with mechanical exfoliation, very few studies are available on large-scale and uniform phosphorene flakes through chemical synthesis. At present, direct chemical growth approach for phosphorene are still inadequate. This may be due to its highly chemical active surface that is fragile when comes in contact with air, as well as lacking of a proper substrate for its CVD growth. Decreasing the air sensitivity of BP is currently under investigation; however, much research has been done with encapsulation and has been shown to be successful with increasing the lifetime of the material. However, the outstanding grown single layer germanene, silicene and stanene with highly chemical active surface on the substrates step up promising possibilities for chemical growth of phosphorene.

### 5. Applications

The exceptional properties of phosphorene have awakened considerable concern and much effort has been dedicated to explore its applications in the field of electronic, batteries, optoelectronics, photovoltaic and so on. The remarkably high footstep of early developments recommends high potential and many more innovative devices for phosphorene applications.

#### 5.1 Field Effect Transistors

Recent decades have seen the steady reduction in size of transistors, presently down to about 20 nm. But this continuous device scaling is impending statical and quantum limits and also experiences difficulties related to heat dissipation. This has triggered the research interest in two dimensional materials for advanced optoelectronic and electronic devices. Graphene, a 2D material has shown extraordinarily high mobility and high breaking strength. However, the zero bandgap in graphene lessen its suitability in semiconducting and optoelectronics devices. Silicene, a 2D layer of silicon atoms, has been considered as semiconducting counterpart of graphene, but its environmental stability represents a key issue for further studies and its applicability. Another 2D semiconductor,
Transition Metal Dichalcogenides (TMDCs) show promising properties for optoelectronics applications but they are suited for applications in only part of the visible range of the electromagnetic spectrum.

Now a day, phosphorene is a promising alternative candidate than silicon-based electronics chips. So, countless transistors could be positioned onto a microchip to present faster and more powerful processors for electronics applications. In 2014, scientists succeed in fabricating field-effect transistors based on few-layer BP crystals with thickness down to a few nanometers. Drain current modulation on the order of $10^3-10^6$ is achieved in samples thinner than 7.5 nm at room temperature, with well-developed current saturation in the I-V characteristics – both are important for reliable transistor performance of the device. Sample mobility is also found high with the highest value up to approx. 1000 cm$^2$/Vs.

In phosphorene-based FETs, conduction channel permits lights with various wavelengths to be exposed to the channel. As phosphorene is highly appropriate to be utilized in the near infrared and night-vision imaging applications, researchers are making efforts to achieve ambipolar performance of BP to construct solar cells and pen junctions and they expect that van der Waals tri-layer phosphorene/TMDC system is a more efficient solar cell than the tri-layer graphene/TMDC systems because the former can benefit from the absorption of wider range of wavelength in the solar spectrum.

Digital electronics highly take advantages of great potential of semiconductors for transistor applications. Accordingly, excellent charge mobility and adequate band gap to achieve a high on/off ratio are the mandatory criteria for high conductivity, operational switching and low power consumption. As a result, 2D materials exhibited inclusive favorable properties as prospective transistor material exclusively phosphorene with controllable band gap of 0.32 eV. Besides, phosphorene’s high charge carrier mobility (1000 cm$^2$/V·s) at room temperature leads to rationally rapid operation. The as-stated properties are substantial in fabrication of transistors with high current density and power gains that are most important characteristics for making high-frequency power amplifiers and high-speed logic circuits.

Recently, the operation of BP Field Effect Transistors (FETs) at gigahertz frequency is demonstrated for the first time. The standard Ground-Signal-Ground (GSG) pads were fabricated to realize the transition from a microwave coaxial cable to on-chip coplanar waveguide electrodes. The measurement result shows that in 300-nm channel length devices, the short-circuit current-gain cut-off frequency $f_t$ is 12 GHz and the maximum oscillation frequency $f_{max}$ is 20 GHz.

The first Radio Frequency (RF) flexible Top-Gated (TG) BP thin-film transistors on highly bendable polyimide substrate for GHz nanoelectronic applications is reported. Enhanced p-type charge transport with low-field mobility $\sim 233$ cm$^2$/V·s and current density of $\sim 100$ $\mu$A/$\mu$m at $V_{DS} = -2$ V were obtained from flexible BP transistor at a channel length $L = 0.5$ μm. Importantly, with optimized dielectric coating for air-stability during microfabrication, flexible BP radio frequency transistors afforded intrinsic maximum oscillation frequency $f_{max} \sim 14.5$ GHz and unity current gain cutoff frequency $f_t \sim 17.5$ GHz at a channel length of 0.5 μm. Notably, the experimental $f_t$ achieved here is at least 45% higher than prior results on rigid substrate, which is attributed to the improved air-stability of fabricated BP devices.

Black phosphorous based transistors have already shown the remarkable performance for RF electronics concerning voltage and power gain owing to the excellent current saturation properties rising from the moderate band gap of BP. Therefore, for operating in the multi-GHz frequency range and beyond, BP is a counted as a prospective potential candidate for upcoming high-performance thin film electronics technology.

### 5.2 Battery Applications

Two dimensional materials are of special interest as host materials for metal ion batteries, due to their unique morphology, which enables fast ion diffusion and offers more ion insertion channels with the whole surface exposed. Actually, the possibility of using various 2D sheets as anodes in LIBs has been explored from the firstly discovered graphene sheet up to the recently synthesized Transition-Metal-Dichalcogenides (TMD) and
MXenes\textsuperscript{97--99}. In view of their flat structures, fast Li diffusion and a large Li capacity can be achieved. However, the weak binding of Li with graphene and other 2D sheets hinders their further applications in LIBs\textsuperscript{100--102}.

As the bulk counterpart of phosphorene, BP has been investigated as a promising candidate for anode materials in LIBs due to its similar structure to graphite also having a strong high capacity of 2596 mA h g\(^{-1}\) and a discharge potential range of 0.4-1.2 V. Additionally, the puckered honeycomb structure of phosphorene is expected to accommodate more Li atoms. The discharge capacity 2786 mA h g\(^{-1}\) obtained at a 0.2 C current rate is higher than that in Li-ion batteries based on germanium, graphite and tin as an anode material. Its constancy is explained with an outstanding result of recycle life test which shows that even after 100 cycles, 80% of capacity is conserved\textsuperscript{43}.

Zhao have examined that Li atoms bind more strongly to double layer phosphorene than monolayer\textsuperscript{103}. The lowest diffusion barrier values of the Li atoms are calculated as 0.76 and 0.72 eV on monolayer and double layer phosphorene, respectively. In addition, the theoretical capacities of Li are found to be 432.79 and 324.59 mA h g\(^{-1}\) for monolayer and double layer phosphorene, which are larger than those of other commercial anodes. In this research, the influence of Si and S implantation is also examined which indicates that Si-doped phosphorene greatly improves the binding of Li atoms, while the diffusion barrier is not affected. These results suggest that phosphorene holds great potential for use in LIBs.

In addition, the superior mechanical properties of phosphorene suggest that phosphorene is rather robust, and structural degradation during the lithiation process is not anticipated which is beneficial for its stable performance as an electrode in LIBs.

### 5.3 In Gas Sensing Devices

Gas sensing device is another future application of phosphorene. The planar structure of phosphorene is highly anisotropic along the armchair and zigzag direction that resulted in unique electrical and optical properties, highly useful for sensing purposes\textsuperscript{36}, which is different from graphene and MoS\(_2\). The adsorption of CO, CO\(_2\), NH\(_3\) and NO\(_2\) on single layers of graphene, MoS\(_2\) and phosphorene are investigated to find their most stable configuration and relative orientations on the host layers and it have been found that the structural and electronic properties of host layers are unaffected as a result of adsorption process. Among these host layers for gas sensing applications, phosphorene indicated the highest physio-adsorption toward all examined molecules due to its controllable electronic properties in optoelectronics and switching devices. Therefore, phosphorene is considered as the most suitable Single Electron Transistor (SET) for gas sensing applications. MoS\(_2\) and phosphorene are found to be additionally sensitive towards the detection of N-based molecules due to the introduction of stronger doping\textsuperscript{104,105}.

### 5.4 As an AM Demodulator

Recent study on BP-based AM demodulator reveals that BP is the most appropriate layered semiconductor candidate in the flexible nanoelectronics field. This is due to its remarkable device performance such as high mobility, excellent current saturation, and ambipolar transport in ambient environment. Recently, scientists have demonstrated the first flexible BP Amplitude-Modulated (AM) demodulator, an active stage useful for radio receivers, based on a single ambipolar BP transistor, which results in audible signals when connected to a loudspeaker or earphone. The BP transistors promote mechanical robustness up to 2\% uniaxial tensile strain and up to 5000 bending cycles. Larger mechanical strains can be accommodated by replacing commonly used high-k dielectric with flexible organic or polymeric gate dielectric. Encapsulated bottom-gated BP ambipolar FETs on flexible polyimide afforded maximum carrier mobility of about 310 cm\(^2\)/V∙s with field-effect current modulation exceeding three orders of magnitude. The device ambipolar functionality and high-mobility were employed to realize essential circuits of electronic systems for flexible technology including ambipolar digital inverter, frequency doubler, and analog amplifiers featuring voltage gain higher than other reported layered semiconductor flexible amplifiers\textsuperscript{106}. 

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6. Challenges and Conclusion

Phosphorene, the new member of two dimensional layered materials family shows many extraordinary properties that have beneficial over those of other 2D layered materials like graphene and TMDCs, because of its high charge mobility and appropriate band gap. Mostly, the current researches focus on applications and device descriptions of phosphorene based on its suitable band gap and high electron mobility. However, phosphorene’s most exclusive features i.e. highly anisotropic structural, transport and electronic properties, have been widely explored, and this lead to new opportunities and possibilities for future research and development.

Further work in this direction may come out with more exceptional performance characteristics of phosphorene over those available in graphene and TMDCs based devices. However, as always, opportunities and challenges go together in the investigation and application of new materials, and such in case for phosphorene. BP can remain stable under ambient environments for many days but single or multi-layer of phosphorene is detected unstable under atmospheric conditions which results in severe degradation caused by some factors such as moisture, oxygen in the air, and molecular HN2. Furthermore, a strong hydrophilic characteristic of phosphorene significantly affects the performance of the manufactured FETs under ambient conditions. Effective schemes are emerging to reduce the structural and property degeneration employing the encapsulation and surface passivation techniques.

The single-layer, double-layer, and multi-layer phosphorene nanoflakes are highly crystalline and unoxidized. Due to a natural band gap of phosphorene, it can be used in manufacturing of electronic devices as an alternative for silicon. Since phosphorene flakes have interesting features including high capacity, superb stability, and high electrical conductivity, they have been found as a very talented material compared to its counterparts for FETs, battery, radio receivers and gas sensing device applications.

Overall, the extraordinary properties of phosphorene make it a future material for designing and fabrication of nanodevices, and more fundamental and technological developments can be established in the near future.

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