Black Phosphorus

Optical and Optoelectronic Properties of Black Phosphorus and Recent Photonic and Optoelectronic Applications

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The rapid development of the semiconductor industry calls for the exploration of novel semiconductors to cater to modern technical and commercial needs. Recently, black phosphorus (BP) has emerged as a new class of 2D semiconducting material and has attracted intensive research attention. The high carrier mobility and tunable direct bandgap of BP deliver great promise in photonic and optoelectronic device applications. Furthermore, the unique intrinsic anisotropy arising from the puckered structure can be exploited in the design of new devices. This review briefly introduces the history of BP and puts emphasis on recent advances pertaining to its optical properties and applications in the photonic and optoelectronic fields. From the perspective of mass production and practical use of BP, some of the research challenges and opportunities are discussed.

1. Introduction

The past few decades have witnessed continuous miniaturization of silicon-based electronic and optoelectronic devices. As devices approach the scale limit, search for novel semiconducting materials to meet modern technological needs is necessary and urgent. To address this issue, 2D nanomaterials come into researchers’ sight and have garnered tremendous research attention.[1–3] Heralded by the discovery of graphene,[4] many types of 2D materials have sprung up, including hexagonal boron nitride (hBN), transition metal dichalcogenides (TMDs), III–VI compounds, and black phosphorus (BP).[5–10] These materials have similar layered structure to graphite so that they can be isolated down to single or several atomic layers. In optoelectronic applications, graphene without a bandgap is not quite suitable for on/off state switching or photodetection. On the other hand, hBN is an insulator with a bandgap larger than 5 eV and its function as a semiconductor is limited as well.[11] Similarly, TMDs such as MoS 2 have low carrier mobility and are indirect semiconductors in their few-layer forms.[5] The III–VI layered materials, such as GaSe and InSe, have direct bandgap even down to few layers and show broadband photoresponse from ultraviolet (UV) to near-infrared (NIR).[12–18] While in the short-wavelength infrared (SWIR) and mid-infrared (MIR) range, BP shows its unique properties and merits as a promising semiconductor for photodetection. Indeed, one distinct advantage of BP, from the perspective of the semiconductor industry, is the direct bandgap which varies from ≈0.3 eV in the bulk to ≈2.0 eV in monolayer, which bridges the “electromagnetic spectrum gap” between graphene and TMDs.[19] The direct bandgap preserved from bulk to monolayer facilitates light–matter interactions. In addition, the direct and moderate bandgap of BP is readily tunable by varying the layer number,[20] strain engineering,[21] chemical tailoring,[22] vertical electric field tuning,[23,24] and so on. The flexible bandgap modulation is expected to spur versatile photonic and optoelectronic applications of BP such as photodetectors and electro-optic modulators with broadband photoresponse spanning the visible and MIR regions.[11,25–27]

Another beneficial feature of BP is the relatively ideal trade-off in the current on–off ratio for carrier mobility. Zhang and co-workers and Ye and co-workers have characterized the electrical transport properties of BP with a nanoscale thickness (=10 nm).[28,29] The mobility of BP-based field effect transistors (FETs) is as high as ≈1000 cm² V⁻¹ s⁻¹ (at room temperature). Although it cannot compare with that of graphene-based FETs, BP outperforms TMDs and even commercial silicon-based devices.[30] The current on–off ratio of BP (=10⁵–10⁷) is four orders of magnitude higher than that of graphene, although it is still several orders of magnitude lower than that of TMDs (=10⁸–10¹⁰).[30] Therefore, from the perspective of FET performance and by considering the two crucial parameters of mobility and on–off ratio, BP bridges the gap between graphene and TMDs. Remarkably, BP FETs exhibit the ambipolar behavior without special treatments which are needed in TMDs.[31–33] This switching behavior between n-type and p-type by gate control renders BP a promising semiconductor in logic devices and photovoltaic applications.[34–36]

BP has strong in-plane anisotropy, similar to other anisotropic layered materials such as WTe₂, ReSe₂, and SnSe.[17] The prominent anisotropy in BP stems from the puckered lattice structure which becomes even more remarkable with reduced dimensionality.[18] This in-plane anisotropy of 2D BP
affects the electrical, optical, thermal, and mechanical properties, thus offering an ideal platform for both fundamental and technical studies that otherwise would not be possible with materials with higher symmetry.

Hitherto there are several review articles on BP regarding its optical and optoelectronic properties and applications. For instance, Huang and Ling mainly focused on the works related to the optical characterization of BP.[7] Besides, Li et al. summarized the recent progress of BP in electronic and optoelectronic devices, such as the BP-based transistors and photodetectors.[39] Still, a comprehensive review article that covers both the optical properties of BP and an overall summary of its applications in photonics and optoelectronics is required. In this review, we summarize recent advances on BP with emphasis on the optical properties and the state-of-the-art applications in the photonics and optoelectronics fields. We first discuss the history and structure of BP focusing on the fundamental optical properties of 2D BP including optical absorption, photoluminescence, photocurrent, third harmonic generation, photocarrier dynamics, and electro-optical modulation. The in-plane anisotropy of 2D BP and recent applications to photonics and optoelectronics are discussed. Finally, the challenges and future research prospects are proposed.

2. Prequel

BP is the most stable phosphorus allotrope, and its history can be traced back to 1914 when Bridgman utilized a high-pressure apparatus to convert white phosphorus to BP at 1.2 GPa and 200 °C.[40] In the following 40 years, this high-pressure synthesis method was the most common way to obtain BP crystals. During this period, scientists experimented with different primary phosphorus allotropes (white phosphorus and red phosphorus (RP)), and by modifying the high-pressure apparatus and transformation processes, BP of different size, morphology, and phase was obtained.[41–45] In the 1960s, an atmospheric-pressure scheme known as the bismuth (or mercury)-flux method to synthesize BP was developed.[46,47] In this method, the melted bismuth is poured onto white phosphorus and purified with 15% HNO₃ followed by steam distillation. After heating to 400 °C for 20 h, the mixture cools slowly to room temperature. After dissolving the mixture with 30% HNO₃, needle- or rod-like BP single crystals (5 × 0.1 × 0.07 mm³) with the needle direction along the a-axis are obtained. This preparation process allows easy doping of silicon, germanium, or tellurium into BP but the reagents are toxic and the process can be time consuming.

To circumvent toxic catalysis or “dirty” flux, chemical vapor transport (CVT) has emerged. In 2007, Lange et al. synthesized high-quality BP crystals from RP by addition of small quantities of gold, tin, and tin iodide at 600 °C at a low pressure.[48] In this method, SnI₄, as the crucial reagent, is prepared by mixing tin and iodine in toluene followed by purification and crystallization. RP, SnI₄, and small amounts of gold and tin are heated to 600 °C for 5–10 days in an evacuated silica ampule. After cooling to room temperature gradually, single BP crystals are obtained. The process can be accelerated by adding SnI₄ and AuSn as precursors to produce crystals larger than 1 cm³[49] and has been optimized by substituting gold with tin to improve the BP quality and reduce the cost.[50]

Owing to the unique properties of BP, there have been a lot of studies on the fundamental properties of bulk BP including the crystal and band structure,[51] electrical and optical properties, as well as superconducting phase transitions.[52–55] Current conduction in BP was first characterized by Bridgman who showed that it was a good conductor with a resistivity below 1 Ω cm.[40] Keyes conducted the electrical conductivity measurements in 1953[52] and Warschauer performed Hall measurements in
1963. Their results show that BP is a p-type semiconductor with a narrow gap of about 0.3 eV. In the 1980s, systematic and comprehensive studies were performed to determine the optical properties of BP by difference techniques such as photoelectron spectroscopy, polarization-sensitive optical absorption and reflectance spectroscopy, and phonon dispersion spectroscopy. BP exhibits phase transitions from the semiconducting orthorhombic phase to the metallic rhombohedral phase at about 5 GPa and to the metallic simple cubic phase at about 10 GPa. In 1968, Wittig and Matthias observed that, at a pressure over 10 GPa, BP turned into a superconductor with a critical temperature \( T_c \) near 4.7 K. This superconducting behavior of BP observed after the findings of superconducting As, S, and I completes the picture that superconductivity is a normal behavior for every truly metallic sp element. These previous studies provide a strong foundation for the present pursuit of BP as a 2D semiconductor.

3. From Bulk to 2D

Inspired by the celebrated discovery of graphene, BP constitutes a new class of 2D materials about a century after the first discovery. Benefiting from its layered structure similar to graphite, BP is cleavable into monolayers. Also, some common and unique characteristics of 2D materials are inherited by BP. The most common way to obtain high-quality few- and single-layer BP is mechanical exfoliation with adhesive tape. Since direct exfoliation cannot always ensure a satisfactory yield of thin BP flakes with a large lateral size, some modification techniques have been proposed to assist the tape peeling method. Castellanos-Gomez et al. employed an intermediate, viscoelastic polymer after exfoliation to increase the yield and reduce contamination on the thin BP surface. Plasma etching has been used to remove the as-cleaved BP layer by layer to obtain thin and large BP flakes under precise control. Liu et al. utilized conductive atomic force microscopy to locally etch BP flakes. After washing (a thinning process), the remaining locally thinned BP exhibited a preserved structure. Although the optimized mechanical exfoliation approach can produce electronic-grade single-crystal BP thin films, the yield is too low and sporadic. In addition, since the process is quite tedious, it is now mainly limited to laboratory use.

In order that 2D BP can be commercially practical, low-cost and large-scale production techniques are crucial. The liquid exfoliation technique used in the preparation of other 2D materials such as graphene and TMDs has been explored to produce BP on the large scale. The liquid exfoliation process relies on two crucial factors, the force to break the interlayer interactions and an appropriate solvent with the suitable surface energy to facilitate delamination while preventing the nanosheets from aggregation or sedimentation. For the former, ultrasonication is commonly used along with the necessary sealing and cooling methods. A shear force can also be employed to break the van der Waals (vdW) forces between layers to improve the yield. For the latter, several organic solvents such as N-methyl pyrrolidone (NMP), N,N-dimethylformamidem (DMF), dimethyl sulfoxide (DMSO), and cumyl hydroperoxide (CHP) have been utilized to prepare BP nanosheets on a large scale. To be environmentally friendly, ionic liquids have been used in lieu of these solvents, and large concentrations of BP nanosheets (=0.95 mg mL\(^{-1}\)) with stability under ambient conditions have been produced. Recently, a low-cost and eco-friendly method known as high-energy ball milling has been developed to exfoliate bulk BP powders into few-layer BP nanosheets by shear force. Unlike liquid exfoliation, ball milling is a totally solid-state mechanochemical process in which anhydrous LiOH is used to avoid unwanted conversion from BP to RP. These liquid exfoliation and ball-milling methods can mass-produce BP thin films with different thickness; however, the lateral size is too small (commonly less than 1 \( \times \) 1 \( \mu \)m\(^2\)) and the quality is unsatisfactory for device fabrication.

To obtain wafer-scale and thickness-controllable 2D BP, numerous efforts have been devoted to exploring bottom-up methods. For example, pulsed laser deposition and thermal vaporization have been proposed to produce BP on different substrates. These large-scale BP films are as thin as 2 nm but the quality is quite compromised by the amorphous feature. Some scientists turned to the traditional high-pressure or CVT method to produce BP thin films in large scale by controlling the reaction time. By evaporating the RP powders at 400 °C followed by the condensation to a flexible substrate, RP thin films with controllable thickness can be formed; these RP thin films can then be converted to BP thin films at high pressure (10 GPa) and room temperature. The obtained BP films are several tens of nanometers in thickness, but the crystalline size is too small (tens of nanometers) and the carrier mobility is low (0.5 cm\(^2\) V\(^{-1}\) s\(^{-1}\)). The RP thin films can also be converted to BP with Sn and SnI\(_4\) as the mineralizing agents in a CVT apparatus. With this method, Smith et al. mass-produced BP thin films with average lateral size and thickness values of =100 \( \mu \)m\(^2\) and tens of nanometers, respectively. Very recently, Li et al. reported the growth of polycrystalline 50 nm BP on sapphire substrates at 700 °C and 1.5 GPa. The thin-film BP is continuous up to 600 \( \mu \)m with the crystal domain size up to 70 \( \mu \)m. More importantly, the field-effect mobility is up to 160 \( \text{cm}^2\text{V}^{-1}\text{s}^{-1}\) at room temperature, which is comparable to mechanically exfoliated BP transistors, suggesting a great leap to the realization of large-scale, high-quality BP devices for practical applications.

4. Structure

4.1. Crystal Structure

BP is a layered crystal similar to graphite, and the intralayer atoms are covalently bonded while the adjacent interlayer atoms are weakly connected by vdW attraction. For convenience, we take the axes of the Cartesian coordinates \((x, y, z)\) to represent the crystal axes \((a, b, c)\), respectively, as depicted in \textbf{Figure} 1a,b. Under ambient conditions, BP has a side-centered orthorhombic structure. Each P atom has five valence electrons in the 3p orbitals, but in a unit cell, it is only bonded to three nearest neighbors, giving rise to sp\(^3\) hybridization. The
three covalent bonds have different bond angles and bond lengths. Two of them are in plane (α = 96.34°, d₁ = 2.224 Å) and the other one is out of plane (β = 102.09°, d₂ = 2.244 Å) (α, β: bond angles, d₁, d₂: bond lengths).[76–78] Owing to out-of-plane distortion, BP shows two inequivalent in-plane directions; the ridge structure along the zigzag direction (y-axis) and puckered structure along the armchair direction (x-axis) thereby producing strong anisotropy of in-plane properties.[37]

4.2. Electronic Band Structure

The electronic band structure of BP calculated by Takao et al. in 1981 reveals a direct bandgap using the tight-binding (TB) approach.[80] In 2000, Asahina and Morita applied the self-consistent pseudopotential method to show that the direct bandgap of BP was ≈0.3 eV at MIR with both valence band maximum (VBM) and conduction band minimum (CBM) located at the Z point.[81] With decreasing thickness from bulk to 2D thin films, BP retains the direct bandgap down to monolayer.[28] In monolayer BP, the original Z point folds back to the highly symmetric Γ point, but the exact top of the VBM slightly deviates from the Γ point with a small value of less than 10 meV. With such a small deviation, monolayer BP can still be considered as a direct bandgap semiconductor.[82] Theoretically, the bandgap of monolayer BP is 1.45–2.0 eV based on a single particle description which ignores the electron–electron interaction and excitonic effects (electron–hole interaction).[21,29,82–84] It should be noted that although the calculation does not take into account the many-body effects and provides insightful results, the excitonic effect is remarkable in BP thin films especially in its monolayer.[20,83,85,86] Experimentally, Liang et al. performed scanning tunneling microscopy to determine that the bandgap of monolayer BP was ≈2.05 eV.[87] For BP thicker than one layer, interlayer interactions cause energy band splitting thus shrinking the energy gap. With increasing thickness, the interlayer interaction becomes stronger and enlarges the band dispersion, leading to a smaller bandgap in thicker BP as shown in Figure 1c.[79,83] Hence, the bandgap declines monotonically and ends up at ≈0.3 eV for the bulk limit.[20] In few-layer BP with strong quantum confinement, the valence and conduction bands split arising from layer–layer interactions are optically discernable and resemble a quantum-well (QW) band structure. In the bulk limit, nevertheless, energy dispersion becomes dense and nonresolvable, and these discrete energy bands turn into quasicontinuous sub-bands.[83,84]

5. Optical Properties

5.1. Layer-Dependent Optical Spectra

The thickness-dependent bandgap can be determined from linear optical absorption spectra.[88–90] Li et al. reported that the optical absorption peaks of hBN-encapsulated BP on sapphire
at 77 K were 1.73 eV for 1 L, 1.15 eV for 2 L, 0.83 eV for 3 L, and less than 0.75 eV for thicker samples, as shown in Figure 2a. Strong photoluminescence (PL) signals detected close to the absorption edge from 1 to 3 L BP are indicative of the direct bandgap of BP.\cite{88} The layer-dependent PL emission also shows that the peak intensity increases dramatically with decreasing layer number even with reduced amount of BP (Figure 2b).\cite{89} For thicker BP (above 30 nm), the absorption edge is in the MIR range (2400 cm\(^{-1}\)), consistent with the \(\approx 0.3\) eV bandgap of the bulk.\cite{90}

To analyze the electronic structure of BP in a more detailed way, Zhang et al. performed absorption measurements from the NIR to MIR range with layer numbers ranging from 2 to 15.\cite{84} Owing to the lowest energy transition, high-index sub-band transitions originating from the nearest neighbor layer–layer interaction are quite pronounced, suggesting a QW-like feature of few-layer BP. According to the tight-binding model and fitted with data from absorption spectra, the transition energy for the \(n\)th sub-bands in \(N\)-layer BP can be described as

\[
E_n^a = 2.12 - 1.76\cos\left(\frac{n\pi}{N+1}\right)
\]

As illustrated in Figure 2c, these multiple sequences of optical resonant peaks provide an efficient tool for thickness characterization by infrared spectroscopy. The lowest energy peaks can be the indicator of the thickness of thinner samples (<5 layers) and the higher energy transition peaks show discernable differences for thicker samples (>5 layers).\cite{84}

Although BP is famous for its MIR bandgap in its few layers to the bulk, the reports on the direct investigation of its PL properties in MIR are still rare. For the first time, Chen et al. have extended the PL measurements of BP to the MIR wavelengths by characterizing 4.5–46 nm thick BP films. The strong PL emission measured at 80 K shows that, with increasing thickness, the bandgap of BP decreasing from 0.441 eV (4.5 nm BP) to 0.308 eV (≈46 nm BP), corresponding to a broad wavelength range in the MIR region from 2.8 to 4 \(\mu\)m. The PL intensity is comparable to that of an InAs multiple quantum well (only several times weaker), suggesting the bright future of BP for the fruition of MIR light-emitting diodes and lasers using 2D-layered materials.\cite{91}

5.2. Anisotropic Optical Properties

The absorption spectra of BP exhibit strong in-plane anisotropy originating from the puckered lattice structure.\cite{37} The calculation shows that the absorption coefficients along the armchair direction is larger than that along the zigzag direction for
thickness from monolayer to bulk, as shown in Figure 3a. This anisotropic optical absorption of BP is ascribed to electron–photon interactions and provides a reliable method for crystalline direction identification. Xia et al. identified anisotropic absorption in few-layer BP based on the polarized-resolved relative extinction spectra. As illustrated in Figure 3b, as the incident light propagates along the \( z \)-direction and the in-plane polarization of the excitation varies, the absorption reaches the maximum for \( x \)-polarized excitation but almost zero for \( y \)-polarized excitation.

The strong anisotropic optical absorption for the lowest energy transition originates from the symmetry selection forbidden rule. The BP crystal possesses an inversion symmetry and mirror reflection symmetry exclusively along the \( x \)-axis, so that the optical transition for electron states located at the \( \Gamma \) point must obey the polarization-conservation rule. That is, the polarized optical absorption can only occur between those bands with identical eigenvalues of the mirror symmetry operator \( M_y \). This requirement is tantamount to that the electromagnetic field of the incident light along \( z \)-direction needs to remain sign-unchanged under mirror reflection and, therefore, the optical transition polarization along the \( y \)-direction is inhibited since the electromagnetic field of the \( y \)-polarized light switches sign under \( M_y \) operation. Theoretically, this polarization-dependent absorption is robust over a wide energy range spanning from 0.33 eV (MIR) up to 3.0 eV (UV). The significant anisotropic optical absorption of BP leads to strong anisotropy manifested in other related optical properties such as the optical contrast, Raman spectroscopy, PL spectroscopy, photocurrent spectroscopy, and photocarrier dynamics.

The anisotropic PL spectra of mono- and few-layer BP are closely related to the anisotropic absorption spectra and share the same symmetry origin. In monolayer BP, the polarization-resolved PL spectra of monolayer BP show nearly perfect linear dichroism. The reduced dimension of ultrathin BP also features a prominent excitonic effect because of the suppressed screening effect and strong Coulomb interaction, giving rise to a high exciton binding energy. Combing the PL and PL excitation (PLE) measurements, the exciton binding energy of monolayer BP is extracted to be \( \approx 0.9 \) eV, consistent with the theoretical energy difference of \( \approx 0.8 \) eV between the quasiparticle and excitonic absorption edges. When the layer number of BP is increased from 2 to 6, the exciton binding energies are 213, 167, 139, 120, and 106 meV according to infrared absorption measurements.

**Figure 3.** Anisotropic optical properties of BP. a) Calculated absorption coefficient \( \alpha \) along the armchair and zigzag directions as a function of excitation photon energy for monolayer, bilayer, trilayer, ten layer, and bulk BP. Reproduced with permission. Copyright 2016, American Chemical Society. b) Polarization-resolved infrared relative extinction spectra when light is polarized along the six directions as shown in the inset. Inset: optical image of a BP flake with a thickness of \( \approx 30 \) nm. Scale bar: 20 \( \mu \)m. Reproduced with permission. Copyright 2014, Nature Publishing Group. c) PL peak intensity as a function of polarization detection angle for excitation laser polarized along \( x \) (gray), 45° (magenta), and \( y \) (blue) directions. Solid lines are fitted curves using a \( \cos^2 \theta \) function (\( \theta \) denotes the angle between the \( x \)-axis and the polarization detection angle). Reproduced with permission. Copyright 2015, Nature Publishing Group. d) Polarization-resolved photocurrent microscopy images of the BP inside the inner ring under illumination at 1500 nm with different light polarizations. The white arrows indicate the excitation polarization directions. Reproduced with permission. Copyright 2014, Nature Publishing Group.
As shown in Figure 3c, the exciton emission peak exhibits strong linear dichroism which favors x-polarization regardless of the excitation polarization. As the polarization angle $\theta$ is varied, the PL peak intensity follows the cos$^2\theta$ rule, and it can be explained by the anisotropic effective mass and strong exciton binding energy in monolayer BP. More specifically, the charge carriers are more mobile along the x-axis due to the smaller effective mass and so the isotropic Coulombic attraction tends to bind excitons along the y-axis, giving rise to strongly polarized excitonic emission.[86]

The highly anisotropic photocurrent in BP is consistent with polarization-selective optical absorption.[93,103] The anisotropic photocurrent has been demonstrated by Yuan et al. for a ring-shaped electrode designed to preclude undesirable linear polarization of the incident light at the electrode edge. The photocurrent intensity is maximized when the incident light is polarized along the x-axis as a direct result of anisotropic optical absorption (Figure 3d). The polarization-sensitive photocurrent response covers a broad range from 400 to 1700 nm with a contrast ratio of 3.5 between the photocurrent magnitude along the two orthogonal polarizations.[91]

While the steady-state optical response is dominated by carriers near the Fermi level, the dynamic counterpart is mostly dependent on the transport of hot carriers.[104,105,110] Ge et al. have characterized linear ultrafast reflection using pump-probe measurements. The relaxation/recombination process of photocarriers is highly isotropic due to the fast (below 200 fs) carrier–carrier scattering. However, the optical conductivity of hot carriers, i.e., excited quasiequilibrium states by the pump light, is highly anisotropic, which may lead to novel device design such as high-speed polarization devices based on BP. The photocarrier lifetime of monolayer BP is characterized to be about 700 ps that is nearly nine times longer than that of the bulk counterpart.[106] The diffusion coefficient $D$ along the zigzag direction is about 16 times smaller than that along the armchair direction. In associated with the isotropic carrier lifetime $\tau$, the carrier diffusion length ($L = (D \tau)^{1/2}$) is four times larger along the armchair direction than that along the zigzag direction.[104]

5.3. Nonlinear Optical Properties

In terms of the nonlinear optical properties, the centrosymmetric crystalline structure of BP only allows third-order nonlinearity.[111,114] Pumped by an ultrafast laser at 1557 nm, strong third-order harmonic generation (THG) at 519 nm can be observed from BP thin flakes. This THG response is highly anisotropic with incident polarization as a direct consequence of the band parameter anisotropy. In addition, the THG signal exhibits significant thickness dependence (Figure 4a) which can be attributed to the strong absorption of THG signals by BP at visible wavelengths along with the interference effects induced by the substrate.[113] Rodrigues et al. have reported that in few-layer BP, the excitonic effects drastically enhance the THG signal which becomes almost one order of magnitude higher than that of graphene.[115]

When the excitation power is sufficiently high, 2D BP shows saturable optical absorption due to the Pauli blocking. That is, when the photoinduced carriers occupy the empty states in the conduction and valence bands, further interband transitions are forbidden, leading to reduced optical absorption just above the bandgap energy with increasing incident power.[9] The intensity-dependent optical transmission is a key factor in the saturable absorber (SA), which is an important nonlinear optical device to convert continuous laser output to a train of laser pulses.[112,113,116–119] Li et al. have reported that the saturable optical absorption of BP exhibits strong layer and excitation polarization dependence. Under 1.55 µm excitation, the saturable absorption reaches the maximum for x-polarized light, which is about three times higher than that for the y-polarized light (Figure 4b). The relative transmittance change is about eight times larger in thicker samples (>1100 nm) than in thinner ones (<25 nm).[112] The saturable absorption properties of BP nanosheets and BP quantum dots (BPQDs) have been verified by Z-scan measurements.[69,113,117,120,121] Owing to the small bandgap, BP shows broadband saturable absorption from visible (400 nm) to MIR region, as shown in Figure 4c.[113,117,122]

5.4. Optical Modulation

BP has excellent optical modulation ability and thus constitutes an attractive material platform for optoelectronics in the NIR and MIR regions. Modulation of the photoresponse of BP can be achieved by applying strain and/or gate biases. Quereda et al. have performed theoretical study to show that in monolayer BP, the shift of the absorption bandedge is up to 0.7 eV under periodic strain (Figure 5a).[123] Compared to 2D TMDs, the energy gap of BP is more sensitive to strain[21] due to the structural difference. In BP with a puckered lattice, the gap is controlled by the in-plane and out-of-plane hopping, and it is more susceptible to in-plane strain.[124] whereas in TMDs, the bandedge states primarily stem from the onsite metal orbitals[126] which are much less sensitive to strain.[127] For optical modulation with gate biases, there are mainly three different mechanisms which have been demonstrated theoretically and experimentally to modulate the bandgap as well as the absorption edge in response to the external electric field on BP. The three mechanisms are the Burstein–Moss shift (BMS) effect, Franz–Keldysh effect, and Stark effect.[124,125,128–130]

In bulk BP, the Franz–Keldysh effect describes the electron and hole wavefunctions leaking into the bandgap under the external out-of-plane electric field, leading to an oscillatory fashion of the interband transition and a redshift of the absorption edge. In 2D BP thin films, strong quantum confinement enables the Franz–Keldysh effect to modulate the inter-subband transitions.[124,128] As BP becomes thinner, the excitonic effect becomes more prominent because of reduced dielectric screening and this phenomenon turns into the quantum-confined Stark (QCS) effect. In 2D BP modulated by vertical electric field through the QCS effect, the opposite shift of VBM and CBM causes shrinkage of the bandgap and reduces the overlap between the electron and hole wavefunctions, giving rise to a redshift of the absorption edge and a reduction of the absorption coefficient.[125] Meanwhile, excitons exist even under the influence of an electric field because separation in
real space between the electrons and holes is limited due to strong quantum confinement. There is another effect in the electro-optic modulation of BP, the BMS effect. In doped BP, when some states close to CBM are populated, the absorption edge shifts to higher energy and the apparent bandgap is increased.\[128\] Therefore, the band-filling BMS effect relies on Pauli blocking and is more pronounced in highly doped materials. On the other hand, the quantum-confined Franz–Keldysh (QCFK) effect is dominant in the low-doping regime where the Fermi level is below CBM.\[124\]

Lin et al. have theoretically investigated the electro-optic properties of BP thin films for optical modulation in the MIR range. As shown in Figure 5b, controlled by the interplay of field-induced QCFK effect and carrier-induced BMS effect, the optical bandgap of BP thin films undergoes blue-, red-, or bidirectional shift, depending on doping concentration, wavelength, and film thickness. In terms of enhanced electroabsorption and reduced power consumption, BP-based optical modulator operating in the QCFK regime outperforms that in the BMS regime, which is also superior to the graphene counterpart.\[124\] Kim et al. have studied the wide-range tuning of \(E_g\) in BP by means of the in situ potassium (K) deposition. By K-doping, the ionized K-donor-induced vertical electric field redistributes the VB and CB wavefunctions to be pulled in opposite directions. This giant Stark effect reduces BP’s \(E_g\) continuously. At a critical dopant density of \(\approx 8.3 \times 10^{13} \text{ cm}^{-2}\), a band inversion occurs and turns BP from semiconductor to Dirac semi-metal.\[23\] Similar to the topological insulator, the band-inverted transition happens when the \(Z_2\) topological invariant changes from 0 to 1.\[131\] Unlike a topological insulator in which the band inversion is caused by strong orbit coupling, in BP it is induced by vertical electric field tuning.

While chemical dopants introduce charge scattering centers and it is difficult to manage reversible doping, electrostatic doping allows for a more controllable approach to tailor the optical bandgap. In 2017, Whitney et al. experimentally explored gate modulation of the infrared photoresponse in few-layer BP.\[128\] Owing to the narrow gap of few-layer BP, an ambipolar BMS shift of the inter-sub-band transitions is observed by transmission measurements. In the heavily doped 6.5 nm BP, BMS shift and QCFK occur, which can be harnessed to build electro-optic modulators. Peng et al. have illustrated that in few-layer BP, the interband and inter-subband absorption in MIR wavelengths shows strong layer and gate dependence, thus making BP a promising candidate in efficient MIR modulators.\[129\] By utilizing the QCS effects and low-temperature scanning tunneling microscopy, Liu et al. have...
shown monotonically reduction of the bandgap with increasing negative gate biases in few-layer BP and the modulation magnitude is up to 310 ± 20 (≈35.5%) in the lightly doped regime (Figure 5c). Deng et al. have experimentally demonstrated that for a 4 nm thick BP, the bandgap shrinkage is limited to ≈75 meV due to strong interlayer coupling. For the 10 nm thick BP, as shown in Figure 5d, the field-induced potential difference is large enough to overcome the interlayer electronic-state coupling, and the bandgap can be continuously tuned from ≈300 to below 50 meV with an external displacement field up to 1.1 V nm⁻¹, consistent with the tight-binding calculation which takes into account the additional bandgap-dependent dielectric screening effect.

6. BP-Based Optoelectronic and Photonic Applications

2D materials have been studied for optoelectronic and photonic applications such as photodetectors, light-emitting diodes, and solar cells. The materials must have high responsivity as well as a short response time over a broad electromagnetic range to cater to industrial needs. Graphene without a bandgap is not attractive for photodetectors and for 2D semiconductors such as TMDs, despite the excellent optoelectronic features, the bandgaps are often too large and limited in the visible range. The direct bandgap only exists in the monolayer forms thereby impeding further optoelectronic and photonic
development. As aforementioned, 2D BP has intrinsic and tunable direct bandgaps in technically appealing wavelengths spanning the visible to MIR regions. Additionally, the significant and unique in-plane anisotropy of BP offers another degree of freedom to store and carry information. Therefore, BP is expected to have a bright future in optoelectronic and photonic applications.[6,7,11,25,132]

Photodetectors can convert information stored in light to electrical signals that can be processed by standard electronic equipment. Because of the direct bandgap and high carrier mobility, BP is promising in building broadband phototransistors for photodetection and imaging.[133–140] The first 2D BP-based photodetector was fabricated by Buscema et al. in 2014. The phototransistors with ultrathin BP (3–8 nm) films show a high photoresponse of 4.8 mA W⁻¹ and fast time response with the rise and fall time to be 1 and 4 ms, respectively. The photoresponse extends from the visible region to NIR (997 nm), showing the broad-wavelength photodetection ability of BP (Figure 6a).[133] In 2015, Wu et al. reported the UV detection capability of BP with high responsivity and specific detectivity (D*) up to 9 × 10⁴ A W⁻¹ and 3 × 10¹³ J, respectively. This strong UV response is ascribed to band nesting along with the unusual high density of states, and the resonant interband transitions between the nested valence and conduction bands result in highly efficient UV absorption (Figure 6b).[134] Because of the narrow bandgap, BP also has the capability in MIR light detection. Guo et al. reported a 10 nm BP photodetector with an external responsivity of 82 A W⁻¹ at 3.39 µm capable of detecting weak light signals at the picowatt level (Figure 6c).[135] Since the optical bandgap of few-layer BP is highly tunable by the QCS effect, the response wavelength range of BP-based photodetectors can be extended by an external vertical electric field. Chen et al. have constructed a tunable MIR photodetector based on high-quality hBN–BP–hBN as shown in Figure 6d. Under a moderate displacement field, the detection region can be extended up to 7.7 µm, which is far beyond the cutoff wavelength of pristine BP. The intrinsic responsivities are 28.7, 1.6, and 0.122 A W⁻¹ at 3.4, 5, and 7.7 µm.[136]

Benefiting from the ambipolar properties of BP, different parts of a single BP flake can be separately tuned into opposite doping regimes to form an artificial PN junction that can utilize the photovoltaic effect (PVE) for photocurrent generation. Buscema et al. have employed two splitting electrostatic top gates with hBN serving as the dielectrics to locally induce electron and hole doping in a few-layer BP as shown in Figure 7a. The gate-defined PN junction exhibits a rectifying Iₘₐₓ–Vₘₜₐₓ behavior and unambiguous photovoltaic response (short-circuit current/open-circuit voltage) under illumination. The responsivity reaches 28 mA W⁻¹ under 532 nm excitation and the power generation wavelength extends to the NIR region of 940 nm.[137] Besides the planar PN junction, Yuan et al. have applied an ionic gel as the gate dielectrics to induce electrons at

![Figure 6. BP-based phototransistor for light detection from UV to MIR regions.](image-url)

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the surface of BP to create a PN junction between the n-doped surface and intrinsically p-doped bulk. The responsivity shows a maximum value of 1.5 mA W$^{-1}$ under 1.7 µm illumination.\cite{93} Liu et al. have demonstrated a PN homojunction diode in a single BP nanoflake by thermally diffusing Al atoms as electron donors for local n-doping (Figure 7b). The diode configuration ensures a significantly suppressed dark current and exhibits a near-identity ideality factor of 1.001 along with a current rectification ratio of 5.6 $\times$ 10$^3$. The short-circuit current responsivity reaches a maximum of 6.4 mA W$^{-1}$ at 1.55 µm.\cite{142} Wang et al. have reported a thickness-modulated all-BP heterojunction phototransistor formed with BP thin films with inhomogeneous thickness in the 6–11 layer range. It shows moderate bandgap difference from $\approx 0.68$ to $\approx 0.40$ eV. Since the VBM and CBM shift in the opposite direction with increasing thickness, the natural heterojunctions with straddling band alignment can be formed at the interfaces of these regions to facilitate dissociation and transport of photocarriers. The device can be operated as a photovoltaic diode with a photoresponsivity of 383 A W$^{-1}$ at 1.55 µm under zero gate bias, and it is among the best photodetectors. For instance, stacking BP with other 2D semiconductors to build functional vdW heterostructures.\cite{146,148} PL quenching has been observed from MoS$\text{$_2$}$–BP and WS$\text{$_2$}$–BP vdW heterostacks, suggesting an efficient exciton dissociation due to the strong built-in electric fields, which is advantageous to optoelectronic applications.\cite{149,150} Deng et al. have stacked mechanically exfoliated p-type BP on n-type CVD grown monolayer MoS$\text{$_2$}$ to construct a PN heterojunction, which shows a maximum photodetector responsivity of 418 mA W$^{-1}$ under 633 nm excitation. The photovoltaic power conversion ability of BP shows an external quantum efficiency (EQE) of 0.35%.\cite{151} Another vertical BP–MoS$\text{$_2$}$ PN heterojunction fabricated with few-layer BP and few-layer MoS$\text{$_2$}$ mechanically cleaved has been reported. The photodetector responsivities are improved to 22.3 A W$^{-1}$ at 532 nm and 153.4 mA W$^{-1}$ at 1.55 µm, respectively. The response time is shortened to 15 µs (rise) and 70 µs (fall) (Figure 8a,b).\cite{144} The BP–MoS$\text{$_2$}$ heterostructure can also be utilized to perform photodetection in the MIR region. Bullock et al. reported the structurally refined BP–MoS$\text{$_2$}$ photodiode, which achieves ultrahigh room-temperature EQE and D$^*$ values of $\approx 35$% and 1.1 $\times$ 10$^{10}$ cm Hz$^{1/2}$ W$^{-1}$ at 3.5 µm, respectively.\cite{152} Different from MoS$\text{$_2$}$, the BP–WS$\text{$_2$}$ heterojunction can be modulated into both anisotype (PN) and isotype (NN and PP) regimes. While tuning into the isotype regime, the heterojunction can serve as an excellent logic optoelectronic device to convert light signal to electronic signal by gate modulation.\cite{153} As a PN diode, the device exhibits photovoltaic properties with an EQE of $\approx 23$% and a responsivity of $7 \times 10^8$ V W$^{-1}$ under 0.4 nW excitation.\cite{154}
In addition to 2D semiconductors, integration of semimetallic graphene into BP for photodetection has been investigated. Liu et al. have fabricated a graphene–BP photodetector in which the bottom layer BP is the light absorption layer and top layer graphene serves as both the carrier transport and passivation layer. Under illumination, photocarriers generated in BP are injected into graphene. The ultrahigh carrier mobility of graphene and suppressed Schottky barrier give rise to efficient photocurrent extraction as exemplified by the ultrahigh photoresponsivity of $3.3 \times 10^3 \text{A W}^{-1}$.[155] The strong in-plane anisotropy of BP can also be utilized in polarization-dependent photodetectors.[145,156,157] In combination with other anisotropic materials such as ReS$_2$, Li et al. have fabricated BP–ReS$_2$ heterostructure for polarized light detection, as shown in Figure 8c. Generation of photocurrent in this heterojunction is managed by the specific alignment of crystal orientation with the AC direction of BP parallel to the $b$-axis of ReS$_2$. When the excitation light is along the AC and ZZ directions, the anisotropy ratio of photocurrent reaches 31 (Figure 8d).[145] These works open new avenues for building novel devices with heterostructures based on materials with different/multiple dimensions.

The important figure of merits of recently developed photodetectors based on BP heterostructures are summarized in Table 1, including all-BP based homo-/hetero-junctions and the integrated structure of BP with other 2D materials. Although the heterostructures based on BP and 1D/0D materials have not been applied to build devices for photodetection yet, the pioneered works on BP–ZnO and BP–CsPbBr$_3$ heterostructures can set the ground for future explorations. These BP-based heterostructures are envisaged to play a vital part in the progress of semiconductor technology.

By integrating BP photodetectors with silicon waveguide (Si-waveguide), the light–matter interaction can be enhanced through the optical confinement in the waveguide and grating structure to overcome the limitation of weak absorption at the cutoff wavelength, thus extending the strong photoresponse to the SWIR and MIR regions.[161–163] Youngblood et al. first reported a Si-waveguide-integrated multilayer BP phototransistor with an intrinsic photoresponsivity of $\approx 135 \text{mA W}^{-1}$ and high response bandwidth exceeding 3 GHz at 1.55 $\mu \text{m}$ (Figure 10a), corresponding to the most useful band in...
telecommunications. The dark current is suppressed by orders of magnitude compared to the graphene counterparts.\cite{ref161} To exploit the plasmonic nanostructure that can confine the optical field to subdiffraction-limited dimensions and drastically enhance the light–BP interaction over a broadband wavelength range, Chen et al. built an on-chip BP photodetector integrated on the Si-waveguide covered by a plasmonic layer. This hybrid architecture combines the advantages of the low propagation loss of Si-waveguide and the high-field confinement of the plasmonic nanogap, affording an intrinsic responsivity of $10 \text{ A W}^{-1}$ and a 3 dB cutoff frequency of 150 MHz at 1.55 $\mu$m (Figure 10b).\cite{ref162} Apart from these photodetectors operating in the telecommunications wavelength, Huang et al. first reported the waveguide-integrated BP photodetector for room-temperature photodetection at MIR region ranging from 3.68 to 4.03 $\mu$m, corresponding to the cutoff wavelength of thick BP with a bandgap of $\approx 0.3$ eV. When the armchair orientation of BP is aligned with the waveguide system, the device achieves its optimal responsivity of $23 \text{ A W}^{-1}$ at 3.68 $\mu$m and $2 \text{ A W}^{-1}$ at 4.03 $\mu$m. The noise equivalent power (NEP) is less than 1 nW Hz$^{-1/2}$, showing good potential for weak light detection.\cite{ref163} Few-layer BP films are capable of photodetection at terahertz (THz) frequencies by integrating with a microscopic FET.\cite{ref25,ref164–168} Because the THz photons do not carry enough energy to excite the bandgap optical transition in BP, signal conversion from optical to electrical must rely on either electronic or thermal effects (e.g., plasma-wave mixing, photo-thermoelectric, and bolometric effects). Viti et al. have examined a THz photodetector based on a 10 nm thick BP flake as shown in Figure 11a. Operated at 0.298 THz, the photodetector exhibits a responsivity of 0.15 V W$^{-1}$ and a NEP of 40 nW Hz$^{-1/2}$ (Figure 11b).\cite{ref164} To achieve good air stability, a BP thin flake is sandwiched between two hBN flakes to form a hBN–BP–hBN vdW heterostructure. This structure elevates the responsivity to $1.7 \text{ V W}^{-1}$ at 0.294 THz. The hBN layer can serve as the ready-to-use gate dielectrics for a gate-tunable THz photodetector.\cite{ref167} By integrating few-layer BP with a log-periodic antenna, Wang et al. have presented a BP photoconductor with ultra-broadband detection from the NIR to the THz range. The device delivers good performance at the THz band with excellent sensitivity (>300 V W$^{-1}$), low NEP (10 pW Hz$^{-1/2}$), and fast response (Figure 11c,d), which are better than those of the graphene counterparts.\cite{ref165} In order to realize a direct sampling of a THz pulse containing both spectral and phase information, Mitten dorff et al. have reported the detection of free-space propagating THz signals by utilizing the photogating effect. The maximum signal-to-noise ratio is on the order of 40 dB at 60 GHz and the...
The saturable absorption feature makes BP thin films and BPQDs very promising as saturable absorbers in ultrafast pulsed fiber lasers. The output pulses are located at the 1.55 μm telecommunication band and are mainly generated by two techniques: Q-switching and mode locking. The performance of BP as SAs is characterized mainly by parameters such as the threshold pumping power, pulse repetition rate, and pulse duration time. By inserting mechanically exfoliated BP flakes into the cavity (length: 11 μm), Li et al. have obtained stable Q-switching pulses from the fiber laser at 1.533 μm with a threshold pump power of 23 mW. The output stability, pulse repetition rate, and maximum pulse energy depend on the pumping power. At a high pumping power, the BP SA is more easily saturated with a larger gain thereby increasing the pulse repetition rate and reducing the pulse duration. In general, the pulse energy increases linearly with pumping power in the appropriate range. As the pumping power is increased, the pulses become unstable or even completely disappear. For a longer cavity length, stable mode-locked pulses can be self-started by introducing disturbance. Utilizing BP nanosheets as SAs, Li et al. have observed a mode-locked pulse output at 1558.7 nm with an ultrashort pulse duration of 786 fs. The soliton-like pulse shape originates from the interplay of group velocity dispersion and self-phase modulation. By using polyvinylidene fluoride–BPQDs as SAs, Xu et al. have reported pulse generation at 1567.5 nm with a real pulse duration of 1.08 ps.

7. Summary and Outlook

The review offers a summary of recent progress on the studies of the optical properties of BP as a 2D layered material and the development of BP-based applications in photonics and optoelectronics. By virtue of the narrow and tunable direct bandgap, high carrier mobility, and remarkable in-plane anisotropy, BP holds great promise for optical applications, especially in the most technically significant wavelengths: the NIR (0.75–1.4 μm), SWIR (1.4–3 μm), and MIR (3–8 μm) regions. To further explore the scientific and technological potential of BP, there are still some challenges to be resolved, and here we provide some research perspectives for future exploration in terms of bringing BP to practical application in photonic/optoelectronic fields.

1) The first obstacle is the lack of reliable and efficient techniques to produce wafer-scale BP with controlled thickness and electronic-grade quality. Top-down methods such as
mechanical cleavage and liquid exfoliation do not seem to work, and bottom-up methods practiced in conversion from RP to BP may offer a brighter future. For example, Li et al. have recently reported the growth of polycrystalline BP on sapphire substrates with large crystal domain size (70 \( \mu \)m) and high mobility at room temperature (160 cm\(^2\) V\(^{-1}\) s\(^{-1}\)).\(^{[75]}\) However, the current on/off ratio is low (\( \approx 9 \)) due to the large thickness (\( \approx 50 \) nm). Since the BP films can be controllably thinned by plasma etching without degrading the electrical performance, the on/off ratio may be optimized by reducing BP to its optimal thickness (\( \approx 10 \) nm) for building transistors to achieve better performance.\(^{[57–59]}\) Also, the conversion temperature and pressure are both high; future work may focus on optimizing these two parameters as well as improving the crystalline quality of BP thin films.

2) The extreme chemical instability of BP can seriously deteriorate the device performance, and hinder the further exploration as well as the wider applications of BP.\(^{[56,169–171]}\) To improve the stability of BP upon ambient exposure, chemical modification and physical encapsulation are common schemes to protect BP from degradation. For the former, organic molecules or metal ions are usually employed to passivate the BP surface and meanwhile modify the optical/electrical properties of BP.\(^{[172–176]}\) For the latter, the atomic layer deposition of dielectric layer such as Al\(_2\)O\(_3\), the spin coating of polymer, or the vdW capping with hBN layer has been developed to provide effective protection.\(^{[177–179]}\) In fact, the best mobility to date of few-layer BP is observed from the hBN–BP–hBN heterostructure.\(^{[180]}\) Benefiting from the reduced scattering centers and charge traps at the interfaces with hBN and effective protection from the outside environment, this sandwiched structure can significantly improve the performance of electrical and optical devices. However, the fabrication procedures such as mechanical exfoliation and microtransfer under vacuum condition tend to be time consuming, and success can be scattered thus not suitable for mass production. Fortunately, since the growth of wafer-scale and high-quality hBN on sapphire and successive transfer to other substrate have been shown,\(^{[181]}\) and the bottom-up synthesis of high-quality BP has made significant progress,\(^{[75]}\) one possible solution is to fabricate wafer-scale BP–hBN with improved electrical properties by using ultraflat hBN substrates. Therefore, fabrication of wafer-scale hBN–BP–hBN heterostructures may be possible. From this perspective, direct synthesis of hBN and BP using the proper transfer procedure to obtain wafer-scale hBN–BP–hBN heterostructure may be a promising pathway to fabricate BP-based devices with high performance and robust chemical stability. In turn, these high-performance devices are conducive for the study of fundamental properties of BP.

3) As we know, BP is a 2D semiconductor featuring its direct and tunable bandgap toward MIR region. The bandgap of thick BP is \( \approx 0.3 \) eV, corresponding to a wavelength of \( \approx 4.1 \) \( \mu \)m. Modulated with the electric field, the response wavelength...
can even extend to 7.7 μm. So far, there are several works on BP-based MIR photodetectors, such as BP phototransistors (3.39 μm),[135] BP–MoS2 photodiodes (3.5 μm),[152] hBN–BP–hBN device geometry with displacement electric field (3.4–7.7 μm),[156] and Si-waveguide-integrated BP phototransistors (3.68–4.03 μm).[161] Among these devices, the sandwiched BP shows broadband photodetection to 7.7 μm, but has to work in cryogenic condition and the fabrication process is rather laborious. The BP–MoS2 photodiode works at room temperature with ultrahigh EQE but relatively low responsivity (0.9 A W⁻¹). The waveguide-integrated BP MIR sensing system exhibits good performance at room temperature, but the carrier mobility may still need further amelioration. In the authors’ opinion, future work can concentrate on achieving higher-performance BP-based MIR photodetectors. In addition, other types of photonic/optoelectronic devices such as optical modulators and lasers that operate in the MIR region can be explored. For example, the research on BP-based light-emitting devices may be promising since BP is recently found to have strong PL emission in the MIR region.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

black phosphorus, in-plane anisotropy, optoelectronics, photonics, 2D materials