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1Polarization Resolved bP / MoS₂ Mid-Wave Infrared Photodiodes with 2High Detectivity at Room Temperature

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15

16 **Infrared (IR) photodetectors are currently subject to a rapidly**
17**expanding application space, with an increasing demand for**
18**compact, sensitive, and inexpensive detectors. Despite continued**
19**advancement, technological factors limit widespread usage of IR**
20**detectors; specifically, the need for cooling and high costs**
21**associated with processing of III-V/II-VI semiconductors. Here, black-**
22**phosphorous (bP) / MoS₂ heterojunction photodiodes are explored**
23**as mid-wave infrared (MWIR) detectors. While previous studies have**
24**demonstrated photodiodes using bP, here we significantly improve**
25**the performance, showing for the first time that such devices can be**
26**competitive with conventional MWIR photodetectors. By optimizing**
27**the device structure and light management, we demonstrate a two-**
28**terminal device which obtains room temperature external quantum**
29**efficiencies (η_e) of 35% and specific detectivities (D^*) as high as**
30 **$1.2 \times 10^{10} \text{ cmHz}^{1/2} \text{W}^{-1}$ in the MWIR region. Furthermore, by leveraging**
31**the anisotropic optical properties of bP we demonstrate the first**
32**bias-selectable polarization resolved photodetector which operates**
33**without the need for external optics.**

34 Infrared (IR) photodetectors are essential components in a host of
35fields, including medical, scientific, communication, automation and
36surveillance.^{1,2} The majority of today's commercially available, high
37performance IR photodetectors are made using III-V and II-VI absorbers, for
38example, In_{1-x}Ga_xAs, InSb, and Hg_{1-x}Cd_xTe.³ While significant progress has

39greatly increased their application, a number of drawbacks limit wider
40utilization of IR photodetectors. Most notably, these devices typically rely on
41expensive growth methods and require active cooling to reduce thermal
42noise. The latter is particularly crucial for narrow bandgap absorbers
43operating in the mid-wave infrared (MWIR, 3-5 μm) and long wave infrared
44(LWIR, 8-12 μm) spectral bands where cryogenic cooling is typically required
45to achieve high performance. In addition, several specific applications cannot
46be directly addressed using detectors fabricated from traditional material
47systems. An example of this is detection of the polarization state of light,
48which is utilized in numerous specialized applications including astronomy,
49polarization-division multiplexing and remote sensing. Normally detectors
50used for this application require either polarization optics or multiple devices
51arranged in a side-by-side configuration, which adds system complexity and
52limits the resolution for imaging purposes. Furthermore, while numerous
53materials, most notably nanowires, show polarized absorption, a polarization
54resolved detector has yet to be demonstrated. As such, there is considerable
55interest in the exploration of new IR absorber materials which offer the
56potential to address these shortcomings and can be applied in novel device
57architectures.

58 Two-dimensional (2D) materials have shown initial promise for use in
59future IR photodetectors.^{4,5} One of the key advantages offered by 2D layered
60crystals is their out-of-plane van der Waals bonding which allows the use of
61thin layers without suffering from detrimental effects such as surface

62dangling bonds. This advantage is particularly important in infrared detectors
63where thin absorbers can reduce noise resulting from generation-
64recombination, a strategy which is often not permitted in traditional
65semiconductors due to surface recombination. Furthermore, the van der
66Waals bonding in these materials allows for the construction of
67heterojunctions without consideration of factors such as lattice matching or
68deposition temperature; providing a significant advantage over traditional
69three-dimensional materials. Black phosphorus (bP), an elemental 2D
70material, has recently garnered a significant amount of attention within the
71optoelectronic community.⁵⁻⁷ This interest is partially based on the
72anisotropic optoelectronic properties of bP, which result in polarization
73dependent absorption.^{7,8} Black phosphorus also exhibits a thickness tuneable
74direct bandgap, between the near infrared ($E_g \approx 1.5$ eV) for monolayers to
75the MWIR ($E_g \approx 0.3$ eV) in the case of bulk.^{7,8} In addition, several studies have
76demonstrated that bP can be effectively combined with transition metal
77dichalcogenides including MoS₂,⁹⁻¹¹ WSe₂,¹² and ReS₂,¹³ to form a range of
78functional van der Waals heterojunctions. To date, numerous photodetectors
79utilizing bP have been demonstrated indicating its promise as a next-
80generation IR detector platform.¹⁴⁻¹⁶ Among these, a number of preliminary
81studies have shown the potential of the bP / MoS₂ heterojunction in this
82application.⁹⁻¹¹ However, devices presented thus far show inferior
83performance to existing IR room temperature photodetectors, with reported
84external quantum efficiency values of less than 5%; and are characterized

85only at discrete wavelengths either in the near infrared or short-wave
86infrared bands.

87 Here we utilize bP / MoS₂ heterostructures to fabricate photodiodes and
88optimize the devices for detection of MWIR light intensity and polarization at
89room temperature. To optimize the collection of light, we perform in-depth
90characterisation of bP, and report, for the first time, the complex refractive
91index of this material in a wavelength range that encompasses the MWIR.
92This information is used to design and fabricate a simple optical structure
93which deliberately utilizes destructive interference to efficiently couple in a
94narrow band of MWIR light – permitting the demonstration of a high quantum
95efficiency bP / MoS₂ photodiode. Finally, we demonstrate a bias-selectable
96polarization resolved bP photodetector, utilizing two orthogonally aligned bP /
97MoS₂ photodiodes, monolithically integrated to create a device which directly
98measures both the intensity and polarization of incoming MWIR light.

99**Results and discussion**

100 **Black phosphorus mid-wave infrared photodiode design.** Two
101primary figures of merit for photodetectors are their external quantum
102efficiency (η_e) and specific detectivity (D^*). These parameters are optimized
103by increasing the percentage of incident photons which generate
104photocurrent as well as via reduction of the electronic noise. As such,
105simultaneous optimization of η_e and D^* requires consideration of both optical
106and electrical design. A schematic showing the structure of the

107heterojunction photodiodes fabricated in this work as well as an example
108optical micrograph are shown in Fig. 1a and 1b, respectively. The device
109consists of a bP / MoS₂ heterojunction where a thin (~10-20 nm) n-type MoS₂
110layer acts as an electron selective-contact and MWIR window. Holes are
111contacted via a rear Au pad, which simultaneously acts as a MWIR back
112reflector. As shown schematically in the simulated band diagram of Fig 1c,
113the MoS₂ heterojunction provides asymmetric band offsets with the bP,
114allowing the flow of electrons to the MoS₂ contact while blocking the flow of
115holes. A false coloured transmission electron micrograph (TEM) of a
116completed device is shown in Fig. 1d. In addition, high resolution TEM images
117of the bP / MoS₂ and bP / Au interfaces are shown in Fig. 1e and 1f,
118respectively. The layered structure of bP and MoS₂ can be seen with
119corresponding monolayer thicknesses of 5.5 Å and 6 Å, respectively. A thin
120amorphous layer can also be observed at both interfaces, most prominently
121at the bP / Au interface, and is attributed to PO_x which forms during device
122fabrication. This layer could potentially improve hole collection at the bP / Au
123interface because of its known p⁺ character which may reduce the hole
124contact resistivity. However, its growth at the bP / MoS₂ interface would
125ideally be avoided to prevent the formation of an electron barrier which
126could result in a reduced collection efficiency.

127 **Refractive index extraction and optical optimization.** Losses due
128to reflection limit the fraction of incident light that can be absorbed and are a
129strong function of both the bP and MoS₂ layer thicknesses. The reflection and

absorption in the device can be modelled utilizing the complex refractive index (n , k) of the two materials. While broadband values of n and k have been reported for MoS₂, only the visible refractive index has been characterized for bP to date.¹⁷ The anisotropic crystalline structure of bP, shown in Fig 2a, results in polarization dependent optical properties (referred to as linear dichroism). Light impinging with an electrical field parallel to the x-axis, or arm-chair direction, sees a sharp absorption onset at the bulk bP band edge of ~ 0.31 eV.^{6,7,18} Absorption of polarized light aligned to the y-axis or zig-zag direction, however, is symmetry-forbidden at the ~ 0.31 eV band edge and substantially weaker at higher energy wavelengths.^{7,8,19} This has been confirmed experimentally for bulk bP from MWIR to visible wavelengths.^{5,7,20} To extract an effective n and k for the x-and y-directions in bP, polarized IR reflection measurements were performed on bP crystals with varying thickness, ranging from 50 nm to 500 nm, on Au substrates. Example reflection data at individual thicknesses is included in Supplementary Information S1. The combined interpolation of these polarized reflection measurements is shown in Fig. 2b and 2c for incident polarisations aligned along the x- and y-axis of bP, respectively.

For polarized illumination aligned to the x-direction, a clear drop in reflection can be seen at photon energies above 0.31 eV for all thicknesses. This is a result of the onset of absorption at the band edge of bP. As expected, no such sharp step is seen for the y-direction in Fig. 2c. Refractive index values are obtained using the transfer matrix method¹⁷ to fit a model

of the thickness (t) dependent reflection $R_{\text{model}}(t)$ to the measured reflection $R_{\text{meas}}(t)$ at each wavelength. The model is based on a bP / Au stack and assumes that the refractive index is thickness independent across the measured thickness range (50 – 500 nm). This assumption is based on the predicted saturation of the layer dependent band-structure of bP above ~ 8 layers,⁶ and also further demonstrated by fitted reflection measurements in Supplementary Material S1. The extracted n and k values for the x-direction and y-direction are provided in Fig. 2d and 2e, respectively. For light polarized in the x-direction a pronounced step in the extinction coefficient, k , is observed at $\lambda = 3.8 \mu\text{m}$ which corresponds well to the expected band edge of bP. More details of the indices extraction process can be found in Supplementary Material S1.

With these n and k values, we use the transfer matrix method to simulate the absorption of the photodiode in the x-direction. Ideally from an electrical standpoint, the thickness of the bP layer should be minimized in order to reduce noise resulting from generation-recombination as well as to improve the carrier extraction efficiency. However, from an optical perspective, absorption within the bP layer, which is small for very thin layers, should be maximised. To obtain a compromise between these two requirements, the bP absorption, averaged between $\lambda = 2.5\text{-}3.8 \mu\text{m}$, is simulated as a function of the bP and MoS₂ layer thicknesses. A contour plot of the modelled absorption is provided in Fig. 2f. The periodic absorption behaviour is associated with changes in front surface reflection due to

thickness dependent constructive and destructive interference of MWIR light. A local maximum in absorption is seen for bP layers with a thickness of 170 nm on Au, with an MoS₂ thickness of zero. This corresponds to the expected quarter wavelength minima in reflection, and hence interference effects can be used to provide a compromise between minimising thickness and maximising absorption. Given that an MoS₂ layer with sufficient lateral conductivity is required to collect electrons, we choose an optimum device configuration of bP (~150 nm) / MoS₂ (15 nm). With this optical design ~80% of incident light polarized in the x-direction at $\lambda = 3 \mu\text{m}$ can be absorbed in the bP layer. We emphasize that, in terms of device thickness, this detector bridges the gap between conventional 2D material photodetectors and traditional bulk semiconductor detectors. Resultantly, it inherits benefits from both of these two detector classes, such as increased absorption as well as being free of surface dangling bonds.

Photodiode characterization. The *IV* characteristics of a typical bP / MoS₂ heterojunction photodiode, measured at 300 K with no illumination, is provided in Fig. 3a and shows the expected rectifying behaviour of a diode formed using a narrow bandgap material. The inset of Fig. 3a compares the measured *IV* behaviour with and without illumination from a 1000 K unpolarized blackbody source. The generation of photocarriers shifts the *IV* curve downwards, resulting in an open circuit voltage V_{oc} and short circuit current I_{sc} , confirming that the device is operating in the photovoltaic mode. Figure 3b shows the relationship between the short circuit current density J_{sc}

199and incident optical power density from a $\lambda = 2.7 \mu\text{m}$ laser diode source. The
200device shows the expected linear increase in photocurrent as a function of
201incident light power density over the full measurement range, which spans
202five orders of magnitude. Similar results are found using a $\lambda = 1.6 \mu\text{m}$
203illumination source as shown in Supplemental Information S5.

204 The quantum efficiency of the device is measured under x -direction
205polarized illumination using a calibrated Fourier transform infrared
206spectrometer (FTIR), the setup of which is described in the Methods section.
207As shown in Fig 3c, the bP / MoS₂ photodiode shows an external quantum
208efficiency η_e of $\sim 30\text{-}35\%$ from $\lambda=2.5\text{-}3.5 \mu\text{m}$. These are the highest η_e values
209reported for bP in this range at room temperature and correspond to current
210responsivity values of $\sim 0.9 \text{ A/W}$ (see Supplemental Information S3). Also
211presented in Fig 3c is the measured reflection R , plotted as $100\%-R$. The
212narrow spectral band of MWIR light coupled into the absorber corresponds to
213the targeted quarter wavelength interference feature with its peak occurring
214just below $\lambda=3 \mu\text{m}$. From η_e and R , the internal quantum efficiency (η_i) can
215also be calculated according to: $\eta_i(\lambda)=\eta_e(\lambda)/(1-R)$, yielding a value of $40\text{-}50\%$ at
216room temperature. The polarization dependence of η_e at $\lambda = 3.5 \mu\text{m}$, as a
217function of polarization angle, is provided in the polar plot of Fig. 3d. It can
218be seen that as the polarization angle is changed from 0° (aligned with the x -
219axis) to 90° (aligned to the y -axis) a decrease in η_e , from greater than 30% to
220less than 1% , is measured. An example $\eta_e(\lambda)$ comparison, across the MWIR
221spectral range, for these two polarization angles is included in the

Supplementary Information S3. That the η_e for x-polarized light is substantially higher than for y-polarized light is consistent with the anisotropic absorption discussed in Fig. 2 and is in alignment with previous responsivity measurements of bP photodetectors at shorter wavelengths.⁷

As shown in Fig. 3e, the η_e shows no significant changes in spectral shape as a function of temperature, apart from a small red-shift in the absorption edge, attributed to a decrease in the bandgap with decreasing temperature. This anomalous temperature dependence of the bandgap has been previously predicted and experimentally observed in bP.^{18,19} However, η_e increases as the temperature is decreased, reaching a value of 63% at 78 K. This is further illustrated in the inset of Fig 3c, with η_e and η_i (measured at $\lambda = 3 \mu\text{m}$) plotted as a function of inverse temperature, showing that η_i reaches a peak value of 84% at 100 K. This is most likely a result of an increase in the minority carrier diffusion length at lower temperature. For a device where the back contact is several minority carrier diffusion lengths (L_d) away from the junction, the internal efficiency can be calculated using:

$$\eta_i = (1 - R(\lambda)) \frac{\alpha(\lambda)L_d}{1 + \alpha(\lambda)L_d} \quad (1)$$

where α is the absorption coefficient. The increase in η_i from 300 K to 77K observed here, is consistent with Hall mobilities measured for bP ($\mu_{h,300\text{K}} \approx 1750 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_{h,77\text{K}} \approx 3,800 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$).²⁴

242 To directly compare the performance of the bP / MoS₂ photodiode to
 243 conventional photodetectors, we extract its specific detectivity D^* . This is
 244 achieved utilizing two independent approaches, which are discussed in detail
 245 in the Methods section. Firstly, D^* is calculated, following the approach
 246 suggested in Ref³ for a photodiode under 0 V bias, from η_e and the zero-bias
 247 resistance area product (R_0A):

$$248 \quad D^* = \frac{\eta_e \lambda q}{hc} \left[\frac{4kT}{R_0A} + 2q^2 \eta_e \Phi_b \right]^{-1/2} \quad (2)$$

249 where λ is the wavelength, q is the elementary charge, c is the speed of light
 250 in vacuum, T is the detector temperature, Φ_b is the background flux density
 251 and h and k are the Planck and Boltzmann constants. The second term in the
 252 parenthesis accounts for contributions to noise from fluctuations in the
 253 thermal background and is negligible in this case, since $4kT/R_0A > 2q^2\eta\Phi_b$.
 254 Figure 3f shows $D^*(\lambda)$ extracted from this approach at room temperature
 255 compared against the current state-of-the-art room temperature
 256 photodiodes,^{21,22} many of which are commercially available. It can be seen
 257 that the bP photodiode outperforms more established technologies in the
 258 MWIR region, with a peak D^* of $1.2 \times 10^{10} \text{ cmHz}^{1/2}\text{W}^{-1}$ at $\lambda = 3.8 \text{ }\mu\text{m}$. It should
 259 be noted that the MoS₂ / bP photodiode presented in Figure 3 has been
 260 characterized at 0 V bias, unlike many of the detectors presented in Figure
 261 3f, which require an applied bias to obtain the reported values. To verify the
 262 MoS₂ / bP photodiode D^* values, the noise equivalent power (NEP) was
 263 measured for this device under flood illumination from a blackbody source as

described in Supplementary Information S4. In this approach the incident power density is calculated using geometrical considerations, the temperature of the source and an integration of the total irradiance to the band edge.²³ Additionally, the noise is directly measured allowing D^* to be calculated as $\sqrt{A \Delta f / NEP}$, where Δf is the integration time (1 second). From this measurement, we find a room temperature D^* value of $7 \times 10^9 \text{ cmHz}^{1/2}\text{W}^{-1}$. This value is in good agreement with the spectral D^* , calculated from the device R_0A shown in Fig. 3f. Further information on the D^* for these detectors, including its temperature dependence, can be found in Supplementary Information S3 and S4.

The frequency response and noise current for the bP / MoS₂ heterojunction photodiodes is characterized in Fig. 4. As shown in Fig. 4a no observable baseline drift in photoresponse is observed under modulated laser diode illumination ($\lambda = 2.7 \text{ } \mu\text{m}$). In addition, the rise and fall times, measured under $\lambda = 2.7 \text{ } \mu\text{m}$ illumination at 0 V bias, are found to be 3.7 μs and 4 μs , respectively as shown in Fig. 4b. These values are among the fastest reported for bP based photoconductors and photodiodes.^{13,15,24} While this is slower than commercially available MWIR photodiodes,²⁹ these values are promising given the early stage of device development and are faster than common photoconductive and thermal detectors, as shown in Supplementary Table S2. The dashed purple lines in Fig. 4b, measured from a commercially available InAs photodiode, are included to provide a reference of the instrument response. Similar rise / fall times are found when

an illumination source of $\lambda = 1.6 \mu\text{m}$ is used, as shown in Supplementary Information S5. Figure 4c shows the measured frequency response, with the -3 dB point at approximately 100 kHz using a $\lambda = 1.6 \mu\text{m}$ illumination source. Figure 4f shows the measured noise current spectrum of the bP / MoS₂ photodiode. The shape it exhibits is commonly seen in systems dominated by generation-recombination noise. Notably $1/f$ noise behaviour is not observed at low frequencies since the device is operated in photovoltaic mode at zero bias.³⁰

Polarization-resolved, bias-selectable photodetector. Finally, we leverage this device structure and the anisotropic optical properties of bP to develop a polarization resolved detector. A schematic of the polarization resolved detector developed in this study is shown in Fig. 5a and a false coloured TEM cross-section of a fabricated device is shown in Fig. 5b. The device consists of two vertically stacked bP layers arranged so that their crystal orientations are perpendicular to one another. These two bP layers are separated by a common MoS₂ electron contact and each bP layer has an isolated hole contact. This configuration is similar to two-colour back-to-back photodiodes which have been previously demonstrated with III-V semiconductors.³¹ The bottom bP layer utilizes a full-area Au hole contact, similar to the photodiodes presented above, while the top bP layer collects holes through a MoO_x / Pd hole contact adjacent to the back reflector. The MoO_x / Pd stack has been shown to be an effective hole contact to a number of semiconductor materials,^{32,33} owing to its large work function.

310 To demonstrate the performance of this device, spectrally resolved
311 photoresponse measurements are taken individually on the top and bottom
312 bP photodetectors using the circuit configuration shown in Fig 5c *i* and *ii*,
313 respectively. Each device is measured under two conditions: linearly
314 polarized light aligned to the x -axis of the top device (90°) and, linearly
315 polarized light aligned to the x -axis of bottom device (0°). All four
316 measurements are provided in Fig. 5d. The performance of this device can
317 be quantified by an extinction ratio r_e for each layer, defined as the
318 photoresponse measured with x -polarized illumination divided by
319 photoresponse for y -polarized illumination. For both the top and bottom
320 devices r_e values of $\sim 100:1$ are calculated at $\lambda = 3.5 \mu\text{m}$, which is on the
321 order of the extinction ratio of the polarizer used in this study. These results
322 are further corroborated by the polar plot of Fig. 5e, which shows the
323 photoresponse as a function of polarizer angle at $\lambda = 3.5 \mu\text{m}$. In separate
324 measurements, presented in Supplementary Information S6, it is shown that
325 the device is also able to simultaneously detect the two linear polarization
326 components when illuminated with unpolarized light. Furthermore, the
327 response from the individual detectors can be accessed in a bias-selectable
328 (*i.e.* two-terminal configuration) as depicted in the circuit schematic of Fig 5c
329 *iii*. By applying a bias of $\pm 250 \text{ mV}$ across the outer contacts one device is
330 reverse biased (where the photocurrent is collected), and the other forward
331 biased (contributing negligibly to the photocurrent). Note that for these
332 measurements the MoS_2 contact was electrically disconnected. The

333 functionality of this configuration is clearly seen in Fig. 5f by the exclusive
334 collection of only 0° or 90° linear polarized MWIR light under negative or
335 positive biasing, respectively. A bias of ± 250 mV was chosen as it was the
336 minimum value at which photocurrent from the two detectors could be
337 effectively separated. Higher biases were avoided to minimise noise due to
338 dark current in the device. The unbalanced photocurrent from the top and
339 bottom bP layers can be attributed to a combination of device variation and
340 differences in absorption arising from the layer thicknesses and their position
341 within the device stack. An optical structure, which couples in and absorbs
342 an equal proportion of perpendicularly polarized light in the two bP
343 absorbers, can be realized by controlling the bP and MoS₂ layer thicknesses
344 and integrating an antireflection layer.

345 **Conclusion**

346 In summary, we have designed and fabricated MWIR bP / MoS₂
347 heterojunction photodiodes with high performance at room temperature. By
348 determining the complex refractive index in the IR, we have designed a
349 simple optical structure for the bP / MoS₂ photodiode that achieves high
350 MWIR absorption via interference. This allows the use of a moderately thin bP
351 layer (~ 150 nm), which reduces noise while still permitting high absorption
352 (in excess of $\sim 80\%$) within a narrow band in the MWIR region. These devices
353 display impressive room temperature η_e and D^* values of 35% and 1.2×10^{10}
354 $\text{cmHz}^{1/2}\text{W}^{-1}$, respectively. Finally, we utilize the anisotropic optical properties
355 of bP to demonstrate a bias-selectable polarization-resolved monolithic

356photodetector, which is capable of simultaneously detecting orthogonally
357polarized light without the use of external optics. This could further be
358expanded upon to create polarimetry focal plane arrays which do not rely on
359moving parts or additional optical components.

360**Methods**

361**Refractive index extraction and optical simulations.** Samples for
362refractive index extraction were fabricated by thermally evaporating Ti / Au
363(5/80 nm) onto a Si/SiO₂ carrier wafer. Following this, bP (Smart Elements)
364was mechanically exfoliated onto the Au surface in an N₂ purged glovebox. A
365set of 22 bP flakes were chosen with approximately linearly spaced thickness
366from 50 to 500 nm, as measured by atomic force microscopy (AFM) (Bruker
367Dimension Icon). Polarized reflection measurements were taken using a
368Fourier transform infrared (FTIR) microscope (Thermo Scientific, Nicolet iS50)
369with a BaF₂ wire grid linear polarizer (Thorlabs). The arm-chair direction of
370the bP absorber was determined by measuring reflection as a function of
371polarization, to find the angle at which maximum absorption occurs. Implicit
372in this approach is the assumption that the largest absorption will occur
373when light is aligned to the x, or arm-chair direction, a fact that has been
374theoretically predicted and demonstrated by a number of previous
375studies.^{7,34,35} In all cases the minimum absorption (at 0.31 eV) was found to
376be offset by 90° from this angle, corresponding to the expected zig-zag or y-
377direction. All FTIR reflection measurements in this study utilize a bare Au
378surface as a 100% reflection standard. The set of reflection curves in the x-

direction were fitted using the transfer matrix method, which models the reflection of the bP / Au stack using the refractive indices of bP as the only fitting parameter. The optical simulations of the full bP / MoS₂ / Au photodiodes were also performed through the transfer matrix method utilizing known refractive index values for Au, constant values for MoS₂ ($n = 4.3$, $k = 0$), as well as the refractive index values for bP measured in this work. An average of the bP absorption values over the $\lambda = 2.5\text{-}3.8\text{ }\mu\text{m}$ range was obtained for every combination of MoS₂ and bP thicknesses.

Device fabrication. Photodiodes presented in this work were fabricated by a dry transfer process utilizing a poly(methyl methacrylate) (PMMA) carrier. A detailed description of this process can be found in Supplemental Information S2. In brief, freshly exfoliated bP and MoS₂ sheets are transferred onto an Au pad creating an Au / bP / MoS₂ stack. A contact to the MoS₂ layer was then patterned by e-beam lithography and a 40 nm thick Ni film was subsequently deposited by thermal evaporation. In some devices, the heterojunction was patterned by e-beam lithography and subsequently etched in a Xactix vapor etching tool by XeF₂.³⁶ Finished devices were encapsulated by an ~ 2 nm thick AlO_x layer formed by thermal evaporation of Al. Example micrographs taken during the above process steps is provided in Supplementary Figure S2. A discussion of the assumptions made for the area of the device is provided in Supplementary Information S2.

For the polarization resolved detector, an identical dry transfer process was used to create an MoS₂ / bP / Au stack. An additional bP flake was transferred

402on top of the MoS₂ layer such that its crystal orientation was orthogonal to
403the bottom bP layer. The crystalline orientations of the bP sheets was
404determined using polarized reflection measurements performed in an FTIR
405microscope as described above. The hole contact for the top bP device was
406patterned using electron beam lithography, followed by evaporation of
407MoO_x / Pd (4/30 nm). For all devices in this study, care was taken to reduce
408air exposure during fabrication of devices to minimize PO_x growth at the bP
409surface. Processing steps including bP exfoliation, lift-off, PMMA removal and
410AFM were all performed in either a glovebox or a nitrogen purged
411environment and all chemicals used were anhydrous. For measurements of
412surface oxidation prevention in fabricated devices please see Supplementary
413Information S3.

414**Device characterisation.** Finished devices were wire-bonded into 24 pin
415chip-carriers which were in turn mounted into a cryostat with a CaF₂ window
416and measured at a base pressure < 10⁻⁵ Torr. Current-voltage measurements
417were taken in a 2-probe configuration, under vacuum using an Agilent
418Technologies B1500A semiconductor device analyser. Spectral response and
419 η_e were characterized at I_{sc} (i.e. 0 V bias) by placing the cryostat at the
420auxiliary exit port of the FTIR. The sample was then excited using modulated
421illumination from a Globar (1000 K blackbody). The resulting photocurrent
422was then sent to a current amplifier (Stanford Research Systems SRS570)
423and subsequently returned to the external detector interface of the FTIR. For
424polarization resolved measurements, a BaF₂ wire grid linear polarizer was

placed in the beam path. The FTIR system was calibrated using two reference detectors: a NIST calibrated Ge photodiode is used to measure the source intensity at the outlet and an inbuilt deuterated-triglycine sulfate (DTGS) detector is used to measure the relative spectral intensity of the source. Further information on the FTIR setup is provided in Supplementary Information S3. Additionally, the detectivity values are confirmed using a blackbody setup with flood illumination. Here the device is excited using a chopper-modulated blackbody (temperature range 473 to 673 K) with no additional optics besides the cryostat window; the incident power density here is calculated using Planck's law and geometrical considerations, *i.e.* aperture size and sample to blackbody distance. Further details on this process can be found in Supplementary Information S4 and in Ref.²³ Reflection measurements are performed in an attached FTIR microscope, with the wire grid polarizer placed in the incoming beam path. The rise/fall times and linearity of the device were characterized using illumination from a $\lambda = 2.7 \text{ }\mu\text{m}$ laser diode. For rise/fall measurements the laser diode was directly modulated with a square waveform, and the instrument response was measured using a commercial InAs photodiode. For frequency response measurements a SRS570 current amplifier in high-bandwidth mode with a gain $>20 \text{ }\mu\text{A/V}$ was used (corresponding to a bandwidth of 1 MHz). For dynamic range measurements the laser was directly modulated at a frequency of 120 Hz. The photocurrent was measured using a lock-in amplifier (Stanford Research Systems SR865). The laser diode intensity was

adjusted over a five order of magnitude dynamic range by controlling the laser current in combination with the use of neutral density filters in the beam path. The 3dB frequency analysis was performed with a $\lambda = 1.6 \mu\text{m}$ laser diode, directly modulated with a sinusoidal waveform.

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463**Author Contributions**

464J.B., M.A. and A.J. conceived the idea for the project and designed the
465experiments. J.B. and M.A. performed optical measurements. M.A., J.B., J.C.,
466and G.H.A. fabricated devices. V.A. performed device simulations. Y.-Z.C. and
467Y.-L.C. performed TEM measurements. J.B, M.A., V.A., V.R.S., Y.G., K.B.C. and
468A.J. analysed the data. J.B., M.A., and A.J. wrote the manuscript. All authors
469discussed the results and commented on the manuscript.

Fig. 1 | bP/MoS₂ heterojunction photodiode. **a**, Schematic of device configuration, showing the heterojunction and contact configuration. **b**, Optical micrograph of a completed device, regions containing bP and MoS₂ are outlined for clarity. **c**, Simulated energy band diagram of the device under equilibrium. **d**, Cross-sectional TEM image of a completed photodiode. **e**, High resolution cross-sectional TEM image showing the bP/MoS₂ interface. **f**, High resolution cross-sectional TEM image showing the bP/Au interface.

Fig. 2 | Infrared optical constants of bP. **a**, Schematic diagram of bP crystal structure, **b**, Reflection of bP on Au, measured for crystals with thickness ranging from 50 nm to 500 nm with the polarizer aligned in the x-direction. **c**, Reflection of bP on Au, measured for crystals with thickness ranging from 50 nm to 500 nm with the polarizer aligned in the y-direction. **d**, Extracted complex refractive index of bP in the x-direction. **e**, Extracted complex refractive index of bP in the y-direction. Error bars in d and e are based on the deviation between the modelled and measured reflection at each wavelength. **f**, Modelled absorption in bP layer, for a bP / MoS₂ stack on Au, as a function of the bP and MoS₂ layer thicknesses.

Fig. 3 | Photoresponse and detectivity. **a**, I/V curve of a bP/MoS₂ heterojunction photodiode; inset shows measurement taken in the dark and under illumination by a 1000 K blackbody source over a voltage range of $V = 495 \pm 50$ mV. **b**, Measured photocurrent as a function of incident illumination intensity. Excitation is performed with a $\lambda = 2.7$ μm laser diode. Error bars are based on the uncertainty in the laser spot size, **c**, spectrally dependent η_e , η_i and 100%- R for a bP / MoS₂ heterojunction photodiode, **d**, measured η_e at $\lambda = 3.5$ μm as a function of polarization angle, **e**, Spectral η_e as a function of temperature. Inset shows η_e and η_i at $\lambda = 3$ μm as a function of temperature. **f**, Specific detectivity as a function of wavelength measured for a bP / MoS₂ heterojunction at room temperature as well as various commercially available and reported MWIR photodetectors. The shaded

504region highlights the MWIR band. All FTIR and laser diode characterization
505was performed at a device bias of 0 V.

506**Fig.**

4

507**Frequency response and noise.** **a**, Photocurrent measured from a bP /
 508MoS₂ photodiode under a modulated illumination source ($\lambda = 2.7 \mu\text{m}$). **b**,
 50990%-10% rise and fall times measured with a $\lambda = 2.7 \mu\text{m}$ illumination source
 510($\sim 10 \text{ mW/cm}^2$). Green solid lines are representative of the bP / MoS₂
 511photodiode and the purple dotted lines show the instrument response
 512(measured using a commercial InAs photodiode, Judson J12D). **c**, Frequency
 513response of a bP / MoS₂ photodiode, showing a 3 dB frequency of 100 kHz
 514($\lambda = 1.6 \mu\text{m}$). **d**, Spectral noise density of a bP / MoS₂ photodiode. All device
 515photoresponse and noise characterization was performed at a bias of 0 V.

516

Fig. 5 | Polarization resolved bP/MoS₂ heterojunction photodiode. **a**, Schematic of polarization resolved bP/MoS₂ heterojunction photodiode, showing the heterojunction and contact configuration. **b**, Cross-sectional TEM image of a completed polarization resolved bP/MoS₂ heterojunction photodetector, showing the various layers in the device. **c**, Electrical configurations used to measure: photoresponse from bP_t (i), photoresponse from bP_b (ii), and photoresponse from the top or bottom mode using the bias selectable mode (iii). **d**, Spectrally resolved photoresponse measured from bP_t and bP_b under linearly polarized illumination normal and perpendicular to the device. **e**, Measured photoresponse under linearly polarized illumination at $\lambda = 3 \mu\text{m}$ in bP_t and bP_b as a function of polarizer angle. **f**, spectrally resolved photoresponse of the device in the bias selectable mode under four

529different conditions: ± 250 mV for polarization aligned to the x-axis of the top
530and bottom devices.

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