INTRODUCTION

State-of-the-art mid-infrared (MIR) detectors are generally made of certain narrow-band gap semiconductors, such as HgCdTe alloys (1, 2) or quantum-well and quantum-dot structures based on group III to V materials (3, 4). Unfortunately, these materials suffer from several major challenges that limit their wide application. First, the growth of these materials is usually sophisticated and environmentally hazardous, making it challenging to flexibly form a heterojunction fabrication processes, resulting in high-cost photodetectors requiring cryogenic operation. We report black arsenic phosphorus–based long-wavelength IR photodetectors, with room temperature operation up to 8.2 μm, entering the second MIR atmospheric transmission window. Combined with a van der Waals heterojunction, room temperature–specific detectivity higher than 4.9 × 10^9 Jones was obtained in the 3- to 5-μm range. The photodetector works in a zero-bias photovoltaic mode, enabling fast photoresponse and low dark noise. Our van der Waals heterojunction photodetectors not only exemplify black arsenic phosphorus as a promising candidate for MIR optoelectronic applications but also pave the way for a general strategy to suppress 1/f noise in photonic devices.

RESULTS

Fabrication of b-AsP phototransistor

We first examined the photoresponse of b-AsP by a phototransistor (as schematically shown in the inset of Fig. 1A). To prevent degradation of b-AsP flakes during the fabrication processes, we prepared b-AsP thin films by mechanically exfoliating bulk b-AsP samples (As₀.8₃P₀.₁₇) onto a highly doped silicon substrate covered by 300-nm SiO₂ in a glove box. We chose flakes of b-AsP ranging from 5 to 20 nm thick for device fabrication due to the desired compromise between high light absorption and low dark current. The devices were then fabricated by standard electron-beam lithography, metallization, and a lift-off process. After the fabrication processes, we spin-coated a thin layer of polymethyl methacrylate (PMMA) to protect the samples from oxidation in the air. Figure 1A shows a typical optical absorption spectrum of the b-AsP samples we used. The absorption peak is located at approximately 2760 cm⁻¹, which corresponds to 3.62 μm. The relatively large thickness plays a beneficial role in boosting the optical absorption and thus the responsivity of the b-AsP–based photodetectors. As the wave number decreases from the peak, the absorption decreases linearly to approximately 1250 cm⁻¹ (corresponding to 8.27 μm), marked by the cross of two red lines (as guides to the eye). These results suggest that the absorption edge is at approximately 1250 cm⁻¹, corresponding to a ~0.15-eV band gap. By combining energy-dispersive spectroscopy with Raman spectra studies, the compositions of the samples were confirmed to be As₀.₈₃P₀.₁₇ (see fig. S1) (21). We also measured the electrical transport of b-AsP field-effect transistors (FETs), the field-effect mobility of which was calculated to be ~307 cm² V⁻¹ s⁻¹ at 0.01-V bias (see fig. S2).
Photocurrent mechanisms of b-AsP

We now turn to study the origin of photocurrent generation in b-AsP. For simplicity and to extract the intrinsic photoreponse, we still use the phototransistor structure. As shown in Fig. 1B, a typical phototransistor (shown in the down inset) exhibits nearly linear $I$-$V$ curves under dark conditions and under the illumination of an 8.05-μm MIR laser. The photocurrent ($I_p = I_{\text{light}} - I_{\text{dark}}$) increased linearly with increasing bias voltage together with the observed zero-biased photoreponse (Fig. 1B, upper inset), suggesting a significant MIR photoreponse. To reveal the detailed photoreponse mechanisms of the devices at the MIR range, we systematically measured the generated photocurrent at various source-drain voltage $V_{ds}$ and gate voltage $V_g$ values, with typical results presented in Fig. 1 (C and D). The photocurrent switched its polarity with increasing gate voltage at all source-drain biases. The opposite photocurrents in different regions are attributed to the photovoltaic (PVE) and photothermoelectric effect (PTE).

At low-doped or intrinsic regimes ($-15 \text{ V} < V_g < 15 \text{ V}$), the photocurrent is positive relative to $V_{ds}$ and reaches a maximum near the charge neutrality point. The positive polarity together with the zero-bias response suggests that the PVE dominates (9, 14, 22–24). In this scenario, the b-AsP/metal Schottky junction plays a key role in the photocurrent generation. Figure 1E schematically shows the photovoltaic response of b-AsP devices in which photogenerated electron-hole pairs are separated at the b-AsP/metal junctions. If the channel is p-type–doped, then the photocurrent is mainly generated at the reverse-biased b-AsP/drain junction (top panel). In the case of slightly n-type–doped b-AsP, the photocurrent is mainly generated at the reverse-biased b-AsP/source junction (bottom panel). Here, $V_{ds}$ is assumed to be positive regardless of the channel type for simplicity. In both cases, the photocurrent is positive relative to the conduction current. We further characterized these junctions through spatial photocurrent mapping measurements (at near-IR range). Figure S3 presents the optical image of the device and corresponding photocurrent mapping results at $V_{ds} = 50$ and 0 mV. The spatial mappings verify that the photocurrent is mainly generated at Schottky junctions. The photocurrent has opposite polarity at the two contacts due to the opposite junction bias direction. The mapping also excludes the photogating effect as the major working mechanism; if photogating dominates the response, then the photocurrent would be mainly generated in the channel center. The PVE is mostly pronounced in the intrinsic
regime due to the lower-channel carrier density and longer photocarrier lifetime.

By contrast, the photocurrent is negative relative to $V_{ds}$ and shows very weak gate dependence in the highly doped regime ($V_g > 15$ V), as shown in the line traces plotted in Fig. 1D. In this case, thermally driven processes (the PTE and bolometric effect) dominate the photocurrent. Unlike in the case of graphene, for which the photocurrent is generated by the bolometric effect only, in b-AsP devices under low source-drain bias, the photocurrent is mainly attributed to the thermally driven processes due to the high electrical conductivity (25–29) and low thermal conductivity (9, 30) of b-AsP. This result can be understood from the expression of the PTE-generated photocurrent: $I_{PTE} = (S_1 - S_2) \Delta T/R_d$, where $\Delta T$ is the temperature gradient, $R_d$ is the resistance of the device, and $S_1$ ($S_2$) is the Seebeck coefficient of b-AsP (metal electrodes). Under higher source-drain biases, the bolometric effect may be pronounced, manifested by a linearly increased photocurrent with $V_{ds}$. Compared with the PVE, the thermally driven processes present a lower responsivity. Therefore, we mainly operated our device in the PVE condition below.

**MIR photoresponse of b-AsP**

Next, we fully characterized the photoresponse of b-AsP in MIR. It is worth mentioning that the large photovoltaic response eventually generates photocurrent under zero source-drain bias through the unapparent asymmetry of metal electrodes or device shape. Higher photoresponses are expected in large built-in filed systems (for example, devices with asymmetric electrodes or p-n junctions). Here, for simplicity, we generally operated devices under zero bias, which also effectively suppresses dark current and therefore power consumption of photodetectors. We measured the zero-biased photoresponse of the b-AsP detectors at the MIR range from 2.4 to 8.05 μm, with typical responsivity data (defined as the ratio of photocurrent to incidence laser power) shown in Fig. 2A [see fig. S4 for results from the visible (0.45 μm) to the near-IR (1.55 μm) range]. Although the responsivity decreases slightly with increasing wavelength of the illumination laser due to decreased optical absorption around the band edges, the device presented a high responsivity (15 to 30 mA W⁻¹) across the entire MIR range tested. To quantify the efficiency of light conversion to current, we extracted the external quantum efficiency (EQE), that is, the ratio of the number of photoexcited charge carriers to the number of incident photons. EQE can be derived by EQE = $(h c I_{P} / e \lambda F)$, where $h$ is the Planck constant, $c$ is the speed of light, and $\lambda$ is the wavelength of the incident laser. The calculated EQE is as high as ~6.1% under the illumination of a 3.662-μm laser, which indicates a promising performance at the MIR range. The speed of response is another important figure of merit of photodetectors; thus, we further measured the response time using a 4.034-μm IR laser, with the results shown in Fig. 2B. The rise/fall time is defined as from 10/90% to 90/10% of the stable photocurrent after turning the laser on/off. The rise time ($\tau_{rise} = 0.54$ ms) and the fall time ($\tau_{fall} = 0.52$ ms) were obtained, as shown in Fig. 2B. Faster photoresponses at typical b-AsP FET devices were observed under the illumination of a 1.55-μm laser with higher power (see fig. S5). In principle, a much faster photoresponse is expected for the PVE. We attribute the relatively slower photoresponse to the percolation transport mode resulting from the imperfect material interface. Namely, the electronic transport turns from a hopping regime at low carrier densities to a band-like regime at high carrier densities. As a result, the photoresponse is slower at low carrier densities (and thus for low incident light power) due to the low mobility and high disorder, which is consistent with the study of Guo et al. (12). Nevertheless, the speed demonstrated here is more than sufficient for IR imaging applications. We further measured the laser power–dependent photocurrent near the absorption peak, with the calculated photoresponsivity and EQE plotted as a function of laser power, as shown in Fig. 2C. The measurements were performed under 3.662-μm MIR laser excitation at $V_{ds} = 0$ V at room temperature. The photoresponsivity decreased from 180.0 to 20.3 mA W⁻¹ as the power increased from 70.1 nW to 44.3 μW (the corresponding EQE decreased from 6.1 to 0.69%), which indicates that the photogating effect plays weaker roles in our illuminating power range due to the trapping centers being saturated under intense light (12).

The puckered crystal structure of b-AsP could naturally yield unique anisotropic photoresponses with many important applications; that is, the photocurrent periodically varies with the polarization of incident light or the current collection direction. Figure 2D shows the measured photocurrent along the $x$- (armchair edge) and $y$-directions (zigzag edge) of the same device (inset of Fig. 2D) at room temperature. The conductivity along the $x$-direction (without light illumination) is approximately 1.73 times higher than that along the $y$-direction at $V_g = 0$ V. This anisotropic factor, $\gamma = I_x/I_y$, is slightly larger than that in black phosphorus (~1.6) (12) and is consistent with previously reported results (20, 25, 31). Under the illumination of a 4.034-μm laser, $I_x/I_y$ is approximately 3.51 at $V_g = 1$ V. We also measured the polarization-resolved photoresponse, whereby the polarization of a linearly polarized incident laser was controlled by a half-wave plate. The polarization-dependent photocurrent mappings are presented in fig. S6. The photocurrent was observed to be maximum when the light polarization was along the $x$-direction and minimum when the light was along the $y$-direction, similar to the observation in black phosphorus (10, 24). The photocurrent anisotropy ratio, $\gamma = (I_{\text{max}} - I_{\text{min}})/(I_{\text{max}} + I_{\text{min}})$, was approximately 0.59, which is larger than that of black phosphorus (~0.3) (24).

**b-AsP based van der Waals photodetector**

High dark current noise is the major challenge of modern narrow-band gap semiconductor–based MIR photodetectors. Next, we demonstrate a general strategy to suppress dark current noise by using 2D van der Waals (vdW) heterojunctions. Integrability is an inherent merit of 2D materials by which different 2D flakes can be sequentially stacked into vdW heterojunctions. High energy barriers naturally formed at the interfaces of vdW junctions can effectively reduce dark noise. Note that this highly desired yet facile strategy simply does not work in traditional materials due to the difficulty of obtaining high-quality heterojunctions.

Following this idea, we fabricated photodetectors based on a b-AsP/MoS₂ heterostructure. The photoresponse of a typical heterostructure device together with its optical image is shown in Fig. 3A. The b-AsP is a p-type semiconductor, whereas MoS₂ is an n-type semiconductor. The typical rectification curves are presented in Fig. 3A, indicating that the vdW p-n junction was formed. This result is further confirmed by the photocurrent mapping at $V_{ds} = 0$ V (fig. S7). The current at the forward bias is more than two orders of magnitude larger than that of under a reverse bias. Because of the energy barrier in the b-AsP/MoS₂ heterostructure, the dark current is markedly depressed. The photoresponsivity and EQE as a function of wavelength are plotted in fig. S8. The photoresponsivity ranges from 216.1 to 115.4 mA W⁻¹ as the wavelength increased from 2.36 to 4.29 μm. The corresponding EQE decreased from 11.36 to 3.33%.

Finally, the current noise density was measured. As shown in Fig. 3B, the noise figure (and thus the detectivity, as discussed below) at the
b-AsP/MoS₂ heterostructure was improved significantly compared with that of the b-AsP FET. The frequency dependence results are also different, reflecting their different dominant noise sources. For the b-AsP FET devices, the 1/f noise prevails at low frequencies (1 to 100 Hz) and is considerably above the Johnson noise level. 1/f noise originates from fluctuations of local electronic states induced by the disorder or defects (32) that generally exist in 2D systems (33, 34). Conversely, for the b-AsP/MoS₂ heterostructure devices, generation-recombination (g-r) noise dominates. g-r noise is caused by the fluctuation of carrier density due to the existence of trapping-detrapping centers. Its noise current spectrum is flat at low frequency and quickly decreases up to a frequency \( f_0 \). As shown in Fig. 3B, the spectrum fits a Lorentzian spectral model well (35, 36) as

\[
\frac{\langle i_n^2 \rangle}{AF} = \frac{A}{1 + (f/f_0)^2}
\]

where \( f_0 = 1/2\pi\tau \) is the 3-dB corner frequency, and \( \tau \) is the lifetime of the trap centers. These results indicate that the energy barrier at the junction efficiently depresses the random transport of the photogenerated carriers and therefore inhibits the undesired 1/f noise. Consequently, using the b-AsP/MoS₂ junction successfully decreased the total noise. Figure 3C shows the favorable NEP (defined by \( i_n/R \), where \( R \) is the responsivity, and \( i_n \) is the measured noise current) obtained from our devices. The room temperature NEP of a junction at the MIR range is below 0.24 pW Hz\(^{-1/2}\), even for 8.05-µm MIR light. With the knowledge of noise density and NEP, another important figure of merit is the specific detectivity, \( D^* \), which determines the minimum illumination light power that a detector can distinguish from the noise. This value can be calculated by \( D^* = (AB)^{1/2}/\text{NEP} \), where \( A \) is the active area of the device, and \( B \) is the measuring bandwidth. The active area is used to normalize the dark noise. Figure 3D shows \( D^* \) as a function of wavelength. For comparison, data from the best available room temperature–operated MIR semiconductor (PbSe-based) detector, bolometer, and thermopile.
are also given in the figure \((37, 38)\). The peak \(D^*\) of our junction approaches \(9.2 \times 10^9\) Jones, and it is consistently larger than \(4.9 \times 10^9\) Jones in the 3- to 5-\(\mu\)m range; these values are well beyond all room temperature MIR photodetectors to date (for example, the black line in Fig. 3D). Actually, the room temperature \(D^*\) of b-AsP FET is considerably larger than \(1.06 \times 10^8\) Jones \((\text{cm Hz}^{1/2} \text{W}^{-1})\) even for 8.05-\(\mu\)m MIR light, which is already higher than that of the commercial thermistor bolometer (the purple line in Fig. 3D). The performance of photodetection shows a significant enhancement for these b-AsP/MoS\(_2\) heterostructure devices.

**DISCUSSION**

In summary, we demonstrated room temperature–operated MIR (entering the second atmospheric transmission window) photodetectors based on b-AsP. Compared with other MIR detectors, such as graphene \((5, 39, 40)\), the b-AsP detectors exhibit significant advantages of promising broadband MIR responsivity, fast speed, and excellent anisotropic photosresponse. In addition, the 2D nature of b-AsP renders it inherently easy to integrate with other materials. The specific detectivity is one of the most important figures of merit for photodetectors. Long-wavelength detection generally requires small-gap semiconductors to absorb light. For junctionless photoconductors, especially for the narrow–band gap 2D materials, poor dark noise causes low signal-to-noise ratio and small specific detectivity. Junctions thus propose an effective approach to enhance specific detectivity considerably. Taking advantage of the promising optical properties of b-AsP and facile fabrication of vdW heterojunctions, we demonstrated that the overall performances, especially the dark current noise and specific detectivity, can be further improved. The main working mechanisms of the devices were also revealed. Further work may include a large-area synthesis of b-AsP thin films and scalable fabrication of MIR devices. Our findings not only exemplify an ideal photodetector for challenging MIR imaging tasks but also pave the way for novel MIR technologies, such as polarization-sensitive detection and free space telecommunication.
MATERIALS AND METHODS

Materials synthesis
BULK b-AsP (AsxP1–x) crystals were synthesized using the mineralizer-assisted short-way transport reaction method (41). Briefly, a mixture of gray arsenic and red phosphorus with molar ratios ranging from 5.5 to 2:8 was used as the precursor. Presynthesized lead iodide (PbI2, weighing 10 mg per 500 mg) was added as the mineralization agent. The mixture was then evacuated in a 10-cm silica glass ampoule and placed horizontally in a furnace. The mixture was heated up to 550°C for 8 hours, held at this temperature for 20 to 80 hours, and slowly cooled to room temperature within 20 hours. In this process, the heating elements of the furnace were configured within the walls. The mixture of reactive materials was located at the hot end, with the empty part of the ampoule toward the cooler center. The arsenic composition, x, obtained by this method is distributed from 0.36 to 0.83. The b-AsP samples with different arsenic compositions were tested in this project, and a typical set of results from the sample with x ~ 0.83 is described in the main text.

Device fabrication
We used a standard mechanical exfoliation method to isolate few-layer black phosphorus flakes, typically ranging from 5 to 20 nm, on a highly doped Si wafer covered by a 300-nm-thick SiO2 layer. The thickness of the flakes was first measured using a Bruker MultiMode 8 atomic force microscope. The b-AsP/MoS2 heterostructure was fabricated using a polymer-free vdW assembly technique in a glove box filled with an inert atmosphere. The devices were fabricated using a conventional electron-beam lithography process followed by standard electron-beam evaporation of metal electrodes (typically 5-nm Ti/50-nm Au).

After the fabrication processes, we spin-coated a thin layer of PMMA to protect the samples from oxidation in air. The stability improvement was verified by checking the optical image, dark current, and photovoltaic response (fig. S9). We did not find any obvious degradation in the protected samples fabricated 2 months ago.

Electrical and photoresponse measurements
Electrical transport and photoresponse measurements were performed using a Keithley 2636A dual-channel digital source meter. The wavelength-dependent photoresponse in Fig. 2A was measured using a custom-built wavelength-tunable multichannel MIR laser source. The spectrum spanned from 2 to 4.3 μm with ~0.43-mm2 spot size. The 5.3- and 8.05-μm light sources were custom-built quantum cascade lasers with ~9-mm2 spot size and ~50-mW power. In the visible- to near-IR range from 450 to 1550 nm, the laser was focused on the device using a 20× objective lens. Noise measurements were performed at room temperature. The devices were set in a thoroughly screened metal box to ensure that the device was working in the dark and to reduce the noise originating from the environment. Noise spectra were acquired by a spectrum analyzer (Stanford Research System SR770, with a measuring bandwidth of 100 kHz) at different biases. All the measurements were performed under ambient conditions.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/6/e1700589/DC1

fig. S1. Raman spectra of b-AsP with different thicknesses.
fig. S2. The transfer curves of two typical b-AsP FET devices.
fig. S3. The photocurrent mappings of a typical device at near-IR range.
fig. S4. The performance of a typical b-AsP device at visible- and near-IR range.
fig. S5. Fast photoresponse at near-IR.

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