AsP/InSe Van der Waals Tunneling Heterojunctions with Ultrahigh Reverse Rectification Ratio and High Photosensitivity

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Van der Waals heterojunctions made of 2D materials offer competitive opportunities in designing and achieving multifunctional and high-performance electronic and optoelectronic devices. However, due to the significant reverse tunneling current in such thin p–n junctions, a low rectification ratio along with a large reverse current is often inevitable for the heterojunctions. Here, a vertically stacked van der Waals heterojunction (vdWH) tunneling device is reported consisting of black arsenic phosphorus (AsP) and indium selenide (InSe), which shows a record high reverse rectification ratio exceeding $10^7$ along with an unusual ultralow forward current below picoampere and a high current on/off ratio over $10^8$ simultaneously at room temperature under the proper band alignment design of both the Schottky junction and the heterojunction. Therefore, the vdWH tunneling device can function as an ultrasensitive photodetector with an ultrahigh light on/off ratio of $1 \times 10^7$, a comparable responsivity of around $1 \text{ A W}^{-1}$, and a high detectivity over $1 \times 10^{12}$ Jones in the visible wavelength range. Furthermore, the device exhibits a clear photovoltaic effect and shows a spectral detection capability up to 1550 nm. The work sheds light on developing future electronic and optoelectronic multifunctional devices based on the van der Waals integration of 2D materials with designed band alignment.

1. Introduction

2D materials have attracted tremendous attentions since the emergence of graphene,[1] later the transition metal dichalcogenides (TMDs),[2–6] black phosphorus (BP),[7–10] and so on.[11–13] Benefiting from the weak van der Waals force, different 2D materials can be vertically stacked to construct the artificial heterostructures, which are often called as van der Waals heterostructures (vdWHs).[14–16] Compared with the conventional epitaxially grown heterostructures, vdWHs hold the advantages of free chemical bond and lattice mismatch at the interface of the stacked 2D materials, which offer the degree of freedom to combine and exploit the unique properties of the component materials in a single device. Through mechanical exfoliation and layer-by-layer stacking or van der Waals epitaxy, various vdWHs with different band alignments and sharp interfaces have been fabricated and studied in a wide variety of...
devices, including atomically thin p–n junction diodes,[17–20] tunneling field effect transistors (TFETs),[21,22] memory devices,[23,24] light emitting diodes,[25,26] and photodetectors.[27–31] Additionally, vdWHs have also been used to create multifunctional devices. Recently, multifunctional vdWHs based on MoS 2 and BP have been demonstrated and shown both high current rectification ratios (≈4 × 10 6) and on/off ratios (≈10 6), which can also function as a tunable multivalue inverter.[32] Another vdWHs consisting of WS 2 /boron nitride (BN)/Graphene with a semifloating gate field effect transistor configuration has been demonstrated as a nonvolatile programmable p–n junction. This type of device has been exploited for memories, photovoltaics, logic rectifiers, and logic optoelectronic circuits.[24] More recently, asymmetric van der Waals heterostructures, composed of graphene, BN, MoS 2, and MoTe 2, have been reported and exhibited a high current on/off ratio of 6 × 10 8 and a rectifying ratio of 3 × 10 9, which can function as a high-performance diode, transistor, photodetector, and programmable rectifier.[33] For a vdWHs p–n junction, the rectifying characteristics is determined not only by the Fermi level difference of the two constituent materials but also the band offset of the conduction band and valence band.[32] However, a low rectification ratio along with a large reverse current is often inevitable for the reported vdWHs diode since the reverse tunneling current is significant considering the ultrathin p–n junction region. This issue is even worse for the atomically thin p–n junction. Furthermore, the high rectification ratio for diodes and high current on/off ratio for transistors usually cannot be achieved simultaneously because of the small band offset as well as the opposite transfer characteristics of the n-channel and p-channel materials.[34–37] These issues can be potentially resolved if a bipolar material with narrow bandgap is chosen as one of the channel materials. Black arsenic phosphorus (AsP), a newly discovered 2D material similar to BP, shows a bipolar characteristic with a narrow bandgap of ≈0.25 eV in bulk crystal form.[38–40] Indium selenide (InSe) is an n-type layered semiconductor with a high electron mobility.[12,14,41] When combining these two materials to form vdWHs, a type-II band alignment with a large band offset of the valence band can be achieved. Moreover, with proper band alignment design of both the Schottky junction and the heterojunction by thickness modulation, the forward current can be significantly suppressed via the synergetic effects of both the Schottky and heterojunction barriers. At the same time, the reverse current can be allowed via the tunneling-dominated transport enabled by the band alignment tuning from type-II to type-III under an external electrical field.

Here, we report a vdWHs tunneling device consisting of AsP and InSe, which can function as a high performance backward diode, transistor, and photodetector. We demonstrate that the tunneling device can achieve a record high reverse rectification ratio exceeding 10 8 and a high current on/off ratio over 10 9 simultaneously (which are among the highest values for a single vdWHs device)[13] at room temperature by gate control. Therefore, the device can be operated as an ultrasensitive photodetector with an ultrahigh light on/off ratio of 1 × 10 8, a comparable responsivity of around 1 A W −1, and a high detectivity over 1 × 10 12 Jones under 520 nm laser illumination. Moreover, a clear photovoltaic effect is observed under zero bias voltage with a short-circuit current as large as 55 nA and an external quantum efficiency (EQE) of 1.5%. In addition, the spectral detection range of the device can extend to 1550 nm, showing the broadband detection capability of the AsP/InSe vdWHs.

2. Results and Discussions

2.1. Optical and Structural Characterizations of the AsP/InSe vdWHs Device

The vertically stacked multilayer AsP/InSe vdWHs was constructed by mechanical exfoliation followed by the polydimethylsiloxane (PDMS)-assisted dry alignment transfer method. The multilayer InSe flake was first mechanically exfoliated onto a SiO 2 /Si substrate, while the multilayer AsP flake was exfoliated onto a PDMS film. Then the AsP flake was precisely transferred onto the surface of the InSe flake on a transfer platform equipped with a micromanipulator and a microscope. Finally, the electrode patterns were defined by electron-beam lithography (EBL) and Cr/Au (15 nm/55 nm) electrodes were deposited by thermal evaporation and a standard lift-off process (more details about the device fabrication are provided in the Experimental Section). Figure 1a,b shows the schematic diagram and optical microscope image of the AsP/InSe vdWHs, respectively. Noted that the electrodes are individually deposited on the InSe and AsP regions, not on the overlapped region. Before measurement, a thin poly(methyl methacrylate) (PMMA) layer was coated on the surface of the device to protect it from exposure to the air. The quality of the AsP, InSe, and heterojunction was confirmed by Raman spectra depicted in Figure 1c. For the pristine AsP thin flake, three main Raman peaks located at 226, 236, and 252 cm −1 can be observed, corresponding to the A 1g , B 1g , and A 2g modes, respectively, which agree well with previous reports of the AsP thin flake.[39] As for InSe flake, one can see four distinct peaks located at 116, 178, 199, and 227 cm −1 , corresponding to the A 1′′(Γ′), E (Γ′′), A 2′′(Γ′′), and A 1′(Γ′) modes, respectively.[41] Moreover, the Raman characteristic peaks of both AsP and InSe can be clearly observed in the heterojunction region with no shift compared to the spectrum of the individual crystal, indicating good quality of each component in the junction region after exfoliation, transfer, and device fabrication process. However, the intensities of the Raman peaks are reduced, possibly attributed to the interfacial coupling between two flakes. Transmission electron microscopy (TEM) of the AsP/InSe vdWHs was conducted and images are shown in Figure 1d,e. The low-resolution TEM image shows a high structural quality of the vdWHs with uniform thickness of each individual layer, and no air bubbles or space gaps are seen at the interface, guaranteeing good electrical connection of the two layers. The layered structure of InSe can be clearly seen with a corresponding monolayer thickness of 8 Å. The disappearance of the layered structure of AsP in this device is possibly due to the unknown crystal axis when the TEM sample was prepared using the focus ion beam (FIB) technique (the layered structure of AsP in another device were shown in Figure S3, Supporting Information). The thicknesses of InSe and AsP layers are obtained to be 10 and 11.5 nm, respectively. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive spectra (EDS) maps of each element were also achieved, as shown in Figure 1f–k.
It is clear that all the constituent elements are distributed uniformly in each layer and no diffusion can be seen except for indium. The diffusion of indium may be caused by the high chemical activity of indium atom and the strong chemical bond between indium and phosphorus or arsenic. Furthermore, the EDS map of oxygen shows no oxidation for both layers since all the preparations of the vdWHs are performed in a N$_2$-protection glovebox (see Figure S1, Supporting Information). Based on the EDS result, the ratio of arsenic to phosphorus is confirmed to be 0.49:0.51 for AsP layer, which agrees with the stoichiometric ratio of the as-grown AsP crystal.

2.2. Electrical Characterizations of the AsP/InSe vdWHs Device

First, the electrical properties of the AsP/InSe vdWHs device as well as the individual AsP and InSe devices were characterized separately. Inset in Figure 2a depicts the schematic diagram of the AsP/InSe vdWHs device for electrical measurements, where the metal contacts on the AsP and InSe act as the drain and source electrodes, respectively, and heavy doped Si as the gate electrode. Figures S4a and S5a in the Supporting Information show the transfer curves of the InSe and AsP FET, respectively. It can be seen that the AsP FET exhibits ambipolar semiconducting behavior with p-type dominance while the InSe FET shows n-type behavior, which are in consistent with previous reports.[39,42] Figure 2a shows the I–V characteristics of the AsP/InSe vdWHs device at a large bias voltage range of $V_{ds} = \pm 5$ V and a gate voltage of $V_g = 10$ V. Surprisingly, a very large reverse current over 10 $\mu$A and an unusual ultralow forward current below pA is observed, indicating a backward diode is formed. The reverse rectification ratio, defined as the ratio of the reverse to forward current, is over $1 \times 10^7$ at room temperature, which is the highest value ever reported for backward diodes. Figure 2d lists the reverse rectification ratio of different backward diodes reported in literature. The reverse rectification ratio of our...
Device is several orders magnitude higher than conventional backward diodes made of bulk materials and vdWHs backward diodes made of other 2D materials. It should be mentioned that the reverse rectification ratio of the AsP/InSe vdWHs diode is thickness dependent, especially the thickness of AsP flake. As shown in Figures S8 and S9 in the Supporting Information, the reverse rectification ratio decreases with thicker AsP flakes.

The gate-dependent $I-V$ characteristics of the AsP/InSe vdWHs device are also measured and shown in Figure 2c. As the gate voltage increases, both the reverse and forward currents increase while the reverse current increases much faster. As a result, the reverse rectification ratio reaches a maximum of $3 \times 10^6$ at $V_g = 10$ V and then decreases monotonically to near 1, as shown in the inset in Figure 2c, indicating a strong gate-dependent rectifying behavior. The high reverse rectification ratio and ultralow forward current indicate that the AsP/InSe vdWHs device can function as a high performance backward diode. The transfer curve of the AsP/InSe vdWHs device at $V_{ds} = -1$ V is depicted in Figure S6d in the Supporting Information. An n-type conducting behavior with a threshold gate voltage of about 10 V, similar to that of isolated InSe, is clearly seen for the vdWHs transistor, indicating that the conducting property of the vdWHs device is mainly determined by the InSe channel at the off state. The transfer curve shows a steep decline at the subthreshold region with a subthreshold swing (SS) of 165 mV dec$^{-1}$ when the gate voltage sweeps from +60 to -60 V, as shown in Figure S7 in the Supporting Information (more discussions about the SS can be found in the Supporting Information). Importantly, a shallow valley emerges around 20 V gate voltage, corresponding to the off-state gate voltage of AsP (see Figure S5, Supporting Information), which means that the screening effect from the underling InSe layer on the upper AsP layer is weak thus AsP can be effectively modulated by gate voltage. The high on-state current over 100 $\mu$A and ultralarge current on/off ratio of $7 \times 10^8$ suggest that the AsP/InSe vdWHs device can be used as a good transistor. It should be emphasized that the vdWHs backward diode in our work is very different from the conventional tunneling p–n diode. For tunneling diodes, the forward current is large, and a negative differential resistance is often present (tunneling diodes are achieved at high gate voltage when thick InSe and AsP layers are used to build the vdWHs, see Figure S9, Supporting Information).

The detailed transport mechanism and gate-modulated rectifying behavior of the AsP/InSe vdWHs backward diode will be explained below based on the band alignment of the AsP and InSe layers.

### 2.3. Tunneling Mechanisms of the AsP/InSe vdWHs Backward Diode

To precisely determine the junction barrier at the interface of the AsP/InSe vdWHs, Kelvin probe force microscopy (KPFM)
is utilized to obtain the Fermi level difference between AsP and InSe by measuring the surface potential. The atomic force microscope (AFM) image was obtained simultaneously, as shown in Figure S10a in the Supporting Information. The surface morphology of the junction area is clean and smooth without obvious air bubbles, demonstrating the high quality of the artificial vdWHs. The thicknesses of AsP and InSe are measured to be 10.8 and 7.7 nm, respectively, which are close to that of the fabricated device. As shown in Figure 3a, the surface potential of AsP is larger than that of InSe, which means AsP has a lower work function compared to InSe. The atomic force microscope (AFM) image was obtained simultaneously, as shown in Figure S10a in the Supporting Information. The surface morphology of the junction area is clean and smooth without obvious air bubbles, demonstrating the high quality of the artificial vdWHs. The thicknesses of AsP and InSe are measured to be 10.8 and 7.7 nm, respectively, which are close to that of the fabricated device. As shown in Figure 3a, the surface potential of AsP is larger than that of InSe, which means AsP has a lower work function compared to InSe. The work function or Fermi level difference is obtained to be about 10.5 mV by the line profile across the heterojunction region. The energy band profiles of Cr, InSe, and AsP prior to contact are shown in Figure 3b, where a type-II band alignment is depicted for the AsP/InSe vdWHs. Based on these results, the energy band diagrams of the AsP/InSe vdWHs device at different bias conditions are shown in Figure 3c–f. At equilibrium state, when AsP and InSe contact with each other, electrons will move into InSe from AsP, leaving more holes in AsP, thus creating a charge carrier accumulation region at the interface with a severe band bending in the InSe side. The energy band diagrams at the metal–semiconductor interface are also shown since a large Schottky barrier is formed at the metal–InSe interface due to the Fermi level pinning effect (see the detailed discussion in the Supporting Information). At small positive gate voltages, $V_g \leq 10$ V, when a negative bias voltage is applied to the AsP side, the built-in electric fields at both the AsP/InSe and metal-InSe interfaces will be counteracted by the external electric field. Therefore, a type-III band alignment is formed at the AsP/InSe interface, which means the electrons can transport from the AsP side to the InSe side via the band-to-band tunneling (BTBT) with the help of the external field. At the same time, the Schottky barrier at InSe–metal interface is reduced, thus a large reverse current is formed in the vdWHs. Generally, the current–voltage relation in the BTBT tunneling model is expressed as

$$I = C_1 V^2 \exp\left(-\frac{C_2}{V}\right)$$

where $C_1$ and $C_2$ are the fitting parameters. As shown in Figure 2b, the reverse current is well fitted by the BTBT tunneling model, confirming the tunneling mechanism of the electron transport under reverse bias for our AsP/InSe vdWHs device. On the other hand, when a positive bias voltage is applied, both the junction barrier and the Schottky barrier are increased, severely hindering the electrons transporting from the source to the drain electrodes. Meanwhile, the large valance band offset at AsP/InSe interface blocks the holes transporting from AsP into InSe. As a result, an ultralow forward current is expected as demonstrated in the $I$–$V$ characteristic of the AsP/InSe vdWHs. However, when the gate voltage increases to be greater than 20 V, the InSe channel becomes very conductive due to the increased electron density and the reduced Schottky barrier (see Figure S4, Supporting Information). Meanwhile, the conductive behavior of AsP transforms from p-type to n-type. Therefore, an n–n junction is formed at the AsP/InSe interface, leading to the large current at both positive and negative bias with a reduced rectification ratio, as seen in Figure 2c.

### 2.4. Photoresponse Properties of the AsP/InSe vdWHs Device

The photoresponse properties of the AsP/InSe vdWHs tunneling device were investigated systematically to examine its potential applications in photodetector and photovoltaic areas. The output characteristics of the device under dark and 520 nm laser illumination with different incident powers are plotted in Figure 4a. Note that all the photoresponse measurements were conducted at zero gate voltage unless otherwise specified. It is evident that the drain current increases significantly at both positive and negative biases under light illumination. Specially, the drain current shows no saturation with increasing bias voltage when $V_{ds} < 0$ whereas a shallow saturation occurs when $V_{ds} > 0$, further verifying the tunneling-dominated current at $V_{ds} < 0$. At zero gate voltage, the InSe channel is highly resistive (see Figure S4, Supporting Information), indicating that most of the bias voltage drops on the InSe channel. Therefore, the photocurrent mainly originates from the photogenerated carriers in the InSe channel moved by the external electric field at a large bias voltage. Inset in Figure 4a is the enlarged $I_{ds}$–$V_{ds}$ curves at small bias voltage. A small negative open-circuit voltage $V_{oc}$ as well as a large positive short-circuit current $I_{sc}$ can be clearly observed under 520 nm laser illumination, demonstrating a photovoltaic effect of the device. The relative small $V_{oc}$ of several mV is mainly due to the small Fermi level difference between AsP and InSe as well as the large resistance of the InSe channel at zero bias condition. Figure S14a in the Supporting Information shows the incident power dependence of the $I_{sc}$ and $V_{oc}$. The $V_{oc}$ increases to 7.2 mV under a
large incident power of 8.8 µW, which is close to the Fermi level difference determined by KPFM. The output electrical power \( P_{\text{el}} \), defined as \( P_{\text{el}} = I_{\text{ds}} \times V_{\text{ds}} \), is extracted from the \( I-V \) curves and plotted in Figure 4b. It is obvious that \( P_{\text{el}} \) increases with increasing incident power. To explain the photovoltaic phenomenon in our device, an energy band diagram of the vdWHs device under 520 nm laser illumination is shown in Figure S15 in the Supporting Information. When the laser is illuminated on the device, electron–hole pairs are generated in both AsP and InSe channels. Under the built-in electric field, the electrons are driven to AsP side whereas the holes to the InSe side and finally collected by the source and drain electrodes, respectively, thus resulting in a negative \( V_{\text{ds}} \) and positive \( I_{\text{ds}} \) as seen in inset in Figure 4a. To rule out the mechanism of the photovoltaic effect, scanning photocurrent mapping is adopted to distinguish the photocurrent generation locations. As shown in Figure 4c, a clear photocurrent is generated in the InSe channel and the junction area near the heterostructure edge, demonstrating the photovoltaic current originates from both the heterojunction and the Schottky junction under zero bias voltage. Generally, the photocurrent \( I_{\text{ph}} \) is defined as the drain current difference under dark and illumination, and light on/off ratio is calculated as \( I_{\text{ph}}/I_{\text{dark}} \). Figure 4d depicts the light on/off ratio as a function of the incident power at \( V_{\text{ds}} = 2 \) V. Surprisingly, an ultraligh light on/off ratio over \( 1 \times 10^7 \) is achieved under 520 nm laser illumination with incident power of 8.8 µW (corresponding to power density of 20 W cm\(^{-2}\)) thanks to the ultralow dark current of the device at \( V_{\text{ds}} = 2 \) V, which, to the best of our knowledge, is the highest value ever reported for photodetectors based on 2D materials and their heterostructures even with the additional help of gate control or ferroelectric field suppression.\(^{[22,33]}\)

To further quantitatively evaluate the performance of the vdWHs photodetector, responsivity, detectivity and EQE are calculated. The responsivity is defined as \( R = I_{\text{ph}}/P_{\text{in}} \cdot A \), where \( I_{\text{ph}} \) is the photocurrent as defined above, \( P_{\text{in}} \) is the incident light power density, and \( A \) is the effective area of the vdWHs device. Detectivity is related to the noise equivalent power (NEP), and defined as \( D^* = (A \cdot \Delta f)^{1/2}/\text{NEP} \), where \( \Delta f \) is the electrical bandwidth. If the shot noise from the dark current is the major contribution to the noise, then detectivity can be expressed as \( D^* = R \cdot A^{1/2}/(2e \cdot \Delta f \cdot I_{\text{dark}})^{1/2} \), where \( e \) is the unit electric charge.\(^{[54]}\) EQE describes the ratio of the number of collected charge carriers to the number of incident photons and can be expressed as \( \text{EQE} = I_{\text{ph}} \cdot h \cdot c/e \cdot h \cdot \lambda \cdot P_{\text{in}} \), where \( h, c, \) and \( \lambda \) are the Planck’s constant, the speed of light, and wavelength of the incident laser, respectively. Figure S14b in the Supporting Information shows the calculated EQE and responsivity of the device in the photovoltaic mode. Both the EQE and responsivity show a weak dependence on the incident power with values of about 1.5% and 6 mA W\(^{-1}\), respectively. Figure 4e displays the responsivity and detectivity as a function of incident power under 520 nm laser illumination at \( V_{\text{ds}} \approx 2 \) V. One can see that the responsivity and detectivity exhibit weak dependence on the incident power with representative values of \( 1 \) A W\(^{-1}\) and \( 1 \times 10^{12} \) Jones, respectively, which are comparable to or greater than conventional Si and GaAs based photodetectors. It is well known that trap states induced photogating effect is frequently observed for photodetectors based on nanostructure materials, such as nanowires and 2D materials.\(^{[35]}\) However, the weak incident

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**Figure 4.** Photoresponse characteristics of the AsP/InSe vdWHs device. a) \( I_{\text{ds}}-V_{\text{ds}} \) curves of the device under 520 nm laser illumination with different power intensities, inset shows the \( I_{\text{ds}}-V_{\text{ds}} \) curves of the device at small bias voltage. b) Output electrical power \( P_{\text{el}} \) versus \( V_{\text{ds}} \). c) Photocurrent mapping of the device under focused 520 nm laser illumination at \( V_{\text{ds}} = 0 \) V. d) Light on/off ratio as a function of incident power under 520 and 1550 nm laser illumination at \( V_{\text{ds}} = 2 \) V. e) Responsivity and detectivity as a function of incident power under 520 nm laser illumination at \( V_{\text{ds}} = 2 \) V. f) Time-resolved photoresponse of the device under 520 nm laser illumination at \( V_{\text{ds}} = 2 \) V.
power dependence of the responsivity suggests that the photogating effect is possibly absent in our vdWHs device. To verify this, we carried out photoresponse measurement of the device at very low illumination intensity (see the results in Figure S12, Supporting Information). A same responsivity of about 1 A W\(^{-1}\) is obtained under weak illumination, even as low as 0.405 nW, demonstrating that the photogating effect is indeed absent for our device. Furthermore, the gate-dependent response of the device was also measured and shown in Figure S13 in the Supporting Information. The photocurrent is significantly modulated by the gate voltage and shows an increase with gate voltage, and so does the responsivity.

Apart from steady state behavior, photo switching and response speed are other important characteristics for high-performance photodetectors. The time-resolved photoresponse of the device to periodically on-off laser illumination was measured. The drain current of the device rises rapidly to a stable value when the 520 nm laser is on and decays quickly when it is off. A good reproducible photoswitching is observed under different laser power levels, as shown in Figures S11 to S13 in the Supporting Information. To accurately determine the response speed of the device, a digital oscilloscope is utilized to record the fast-varying photocurrent signals. Figure 4f and Figure S14d in the Supporting Information display the time-resolved photocurrent of the device at \(V_{ds} = 2\) and 0 V, respectively. The response speed, usually represented by rise time (or decay time), is defined as the time it takes for the net photocurrent to increase from 10% to 90% (or decrease from 90% to 10%). Rise time of 217 \(\mu\)s and decay time of 89 \(\mu\)s are obtained at \(V_{ds} = 2\) V for our device, indicating the fast separation of the photogenerated electron–hole pairs under the external electric field. The fast rise and decay times further demonstrate the absence of the photogating effect for our device. However, when the device is operated in the photovoltaic mode, the rise and decay times increase to 620 and 430 \(\mu\)s, respectively. The slower response speed can be attributed to the longer transit time for the carriers to cross the channel because of the high band offset of the valence band. At the metal–InSe Schottky junction, the photoexcited hot electrons in the metal can cross over the Schottky barrier to InSe channel because of the high band offset of the valence band.

In summary, we have successfully fabricated a vdWHs tunneling device based on AsP and InSe 2D materials and demonstrated that the device can function as a high-performance backward diode, transistor, and photodetector attributed to the unique band alignment of the heterostructure. Specifically, a record high reverse rectification ratio exceeding 10\(^7\) and a high current on/off ratio over 10\(^8\) are achieved simultaneously by gate control at room temperature. More importantly, the vdWHs device exhibits an ultrasensitive photodetection capability with an ultrahigh light on/off ratio of 1 \(\times\) 10\(^7\), a comparable responsivity of around 1 A W\(^{-1}\), and a high detectivity over 1 \(\times\) 10\(^{12}\) Jones in visible wavelength range. Furthermore, the device shows a clear photovoltaic effect and can detect near infrared light up to 1550 nm. Our work paves the way to develop future electronic and optoelectronic multifunctional devices based on the van der Waals integration of 2D materials.

3. Conclusion

In summary, we have successfully fabricated a vdWHs tunneling device based on AsP and InSe 2D materials and demonstrated that the device can function as a high-performance backward diode, transistor, and photodetector attributed to the unique band alignment of the heterostructure. Specifically, a record high reverse rectification ratio exceeding 10\(^7\) and a high current on/off ratio over 10\(^8\) are achieved simultaneously by gate control at room temperature. More importantly, the vdWHs device exhibits an ultrasensitive photodetection capability with an ultrahigh light on/off ratio of 1 \(\times\) 10\(^7\), a comparable responsivity of around 1 A W\(^{-1}\), and a high detectivity over 1 \(\times\) 10\(^{12}\) Jones in visible wavelength range. Furthermore, the device shows a clear photovoltaic effect and can detect near infrared light up to 1550 nm. Our work paves the way to develop future electronic and optoelectronic multifunctional devices based on the van der Waals integration of 2D materials.

4. Experimental Section

Device Fabrication: The AsP/InSe vdWHs devices presented in this work were fabricated by a common dry transfer method utilizing a PDMS carrier. First, thin InSe flakes were exfoliated from the commercial bulk counterparts (2D Semiconductors, America) using Scotch tape and then transferred onto a silicon substrate (with 300 nm SiO\(_2\)). Then, thin AsP flakes were exfoliated onto the PDMS film from an as-grown AsP crystal and transferred onto the InSe flake under the optical microscope assisted by an aligned transfer system. All the processes were conducted in the \(N_2\)-protection glovebox to minimize the oxidation of InSe and AsP. To fabricate the device for measurements, electrode patterns were defined by EBL (FEI F50 scanning electron microscopy (SEM) with nano pattern generation system (NPGS) system) and Cr/Au (15 nm/55 nm) metals were deposited by thermal evaporation and
standard lift-off process. To improve the long-term stability, a PMMA layer was coated on the surface of the device soon after fabrication to protect it from exposure to air.

**Device Characterizations:** Morphology of the AsP/InSe vdWHs was investigated by an optical microscope (BX51, OLMPUS). Raman spectra were achieved at room temperature by a confocal Raman/luminescence (PL) system (LabRAM HR800) equipped with 532 nm laser source. High resolution transmission electron microscopy (HR-TEM) images and EDS maps were acquired utilizing FEI Titan Probe microscope system. The TEM specimens were prepared by FIB technique using an FEI Helios SEM system with a Ga ion source. The thickness and surface potential of the layers were obtained by AFM and KPFM characterizations (Bruker Multimode 8). The electrical properties of the fabricated devices were measured in a probe station (Lake Shore) using a semiconductor measurement system. All the devices were monitored the time dependence of the current. For infrared photoresponse measurements, the devices were measured in a probe station (Lake Shore) using a semiconductor measurement system.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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F.W. and H.X. contributed equally to this work. W.D.H. and J.L.W conceived and supervised the project. F.W. fabricated the devices and performed the electrical and photoresponse characterizations. H.X. performed the KPFM measurements. X.W., H.D.S. and J.W.Z. performed the TEM characterizations. L.C. and W.C.R. provided the AsP bulk crystals. F.W., H.X. contributed equally to this work. W.D.H. and J.L.W conceived the paper. This work was supported by the National Natural Science Foundation of China (Grant Nos. 61674157, Key Research Project of Frontier Science of Chinese Academy of Sciences (CAS):QYZDB-SSW-JSC031, CAS Interdisciplinary Innovation Team, Natural Science Foundation of Shanghai (Grant Nos. 18ZR1445800, 18ZR1445900), the CAS Pioneer Hundred Talents Program and the China Postdoctoral Science Foundation (Grant No. 2018M632171).

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

backward diodes, photodiodes, rectification, tunneling, van der Waals heterojunctions

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