Role of Metal Contacts in High-Performance Phototransistors Based on CVD WSe₂ Monolayer

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ABSTRACT:

Phototransistors based on monolayer transition metal dichalcogenides (TMD) have high photosensitivity due to their direct band gap transition. However, there is a lack of understanding of the effect of metal contacts on the performance of atomically thin TMD phototransistors. Here, we fabricate phototransistors based on large-area chemical vapor deposition (CVD) tungsten diselenide (WSe₂) monolayers contacted with the metals of different work function values. We found that the low Schottky-contact WSe₂ phototransistors exhibit a very high photo gain (10⁵) and specific detectivity (10¹⁴Jones), values higher than commercial Si- and InGaAs-based photodetectors; however, the response speed is longer than 5s in ambient. In contrast, the response speed of the high Schottky-contact phototransistors display a fast response time shorter than 23ms, but the photo gain and specific detectivity decrease by several orders of magnitude. Moreover, the fast response speed of the high Schottky-contact devices is maintained for a few months in ambient. This study demonstrates that the contact plays an important role in TMD

phototransistors, and barrier height tuning is critical for optimizing the photoresponse and photoresponsivity.

KEYWORDS: Photodetector • Contact effect • Schottky barrier • Tungsten diselenide • **2d material**

The monolayer two dimensional (2D) transition metal dichalcogenides (TMDs) are potentially important building blocks for nanoscale optoelectronics due to their unique optical properties.¹⁻⁹ Recently, there has been much interest in the molybdenum disulfide (MoS₂) monolayer because of its direct band gap of ~1.8eV,¹⁰ excellent ON/OFF current ratio of 10⁸,¹¹ high photo gain of 5000,¹² and high specific detectivity of 10¹⁰-10¹¹Jones.¹³ However, the response time of the reported MoS₂ phototransistors for either exfoliated or CVD synthesized MoS₂ varies from < 1ms to >30s.^{2,12-16} Distinctly different photoresponse behaviors at the ON state of MoS₂ phototransistors have also been observed. Kim et al. found that there was no photocurrent at the ON state.^{13,16} In contrast, Kis et. al. presented a high photocurrent at the ON state for MoS₂ phototransistors.^{2,12,14} In addition, most of groups attributed the photocurrent to the separation of photogenerated electron-hole pairs at the metal/semiconductor interface.^{2,12-16} However, Castellanos-Gomez's group claimed that the photocurrent is dominated by the photothermoelectric effect for their ohmic-contact MoS₂ phototransistors.^{17,18} The Schottky contact between semiconducting channels and metallic electrodes plays an important role for a conventional photodetector based on the metal-semiconductor-metal structure.¹⁹ Many groups tentatively attributed the different electrical and optical transport properties to the Schottky contacts.^{2,12-18} However, there is still no systematic research on the role of the metal contact in

photodetectors based on atomically thin TMD layer materials.

As MoS₂ films on SiO₂/Si substrates are heavily *n*-doped by defects, charged impurities and adsorbates, it is difficult to tune the Schottky barrier height at the interface between MoS₂ channels and metallic electrodes.^{20,21} Nevertheless, we have recently synthesized highly quality crystalline and large-area tungsten diselenide (WSe₂) monolayers on sapphire by the CVD method,²² and successfully transferred the monolayer WSe₂ films to SiO₂/Si substrates. The monolayer films display strong photoluminescence, opening up potential applications in optoelectronics. Using the transferred CVD WSe₂ monolayer films as channels, we fabricate monolayer WSe₂ transistors and systematically study the Schottky contact effect on the electrical and optical transport properties of atomically thin TMD materials. We demonstrate low Schottky barrier *p*-type transistors with an ON/OFF current ratio of up to 10⁹ and mobility larger than 7.3cm²/Vs using high work function Pd metal contacts. The external photo gain of the Pd-contacted monolayer WSe₂ device is up to 3.5×10⁵ and the specific detectivity is higher than 10¹⁴ Jones. However, the photocurrents for the Pd-contacted devices take more than 5s to saturate in ambient air. In contrast, the high Schottky-barrier WSe₂ devices using low work function Ti metal contacts present a much faster response time of <23ms, and better photocurrent linearity as a function of incident optical power. We suggest a qualitative mechanism based on metal/semiconductor junction energy band diagrams to explain these distinctly different phenomena.

RESULTS AND DISCUSSION

The large area WSe₂ monolayers were grown on sapphire by the vapour-phase reaction of WO₃ and Se powders in a hot-wall CVD chamber as described in our previous work.²² After growth, the films were transferred to 300nm SiO₂/Si substrates. Figure 1a shows the optical

image of a $\sim 1 \times 1$ cm transferred film on SiO_2/Si substrate, and Figure 1b is the magnified optical image with no obvious optical contrast difference across the field, indicating that the transferred film was uniform.²³ Atomic force microscopy (AFM), Raman spectroscopy, and photoluminescence (PL) were used to characterize the number of layers and quality of the transferred films. As shown in Figures 1c and 1d, the representative thickness of the transferred films is ~ 0.97 nm, which is slightly thicker than the as-grown monolayer WSe_2 on SiO_2/Si ,^{22,24,25} and this could be attributed to residual chemical contamination of the transferred process or the substrate effect.²⁶ The Raman spectra for the transferred films excited by a 473 nm laser are shown in Figure 1e, where two characteristic peaks at 248 cm^{-1} and 259 cm^{-1} are observed. According to the calculated phonon dispersion and experimental studies of monolayer WSe_2 , the peak at 248 cm^{-1} is assigned to the in-plane vibrational E_{2g}^1 mode.²⁷⁻³² However, there are different assignments in the literature for the peak at $\sim 259 \text{ cm}^{-1}$. Some papers attributed it to the out-of-plane A_{1g} mode,²⁷⁻²⁹ while others assign it to second order longitudinal acoustic phonons at the M point ($2\text{LA}(\text{M})$) in the Brillouin zone.^{30,31} Regardless of assignment, the Raman spectra of our transferred films are consistent with that of mechanically exfoliated natural WSe_2 monolayers. In addition, the strong PL of the WSe_2 film implies a highly radiative recombination rate, in agreement with the direct band transition for the WSe_2 monolayer. The typical peak position of the PL spectrum is ~ 763 nm, corresponding to a band gap of ~ 1.63 eV.³² All optical images, AFM, Raman and PL spectra confirm that the transferred film is high-quality WSe_2 monolayer.

Figure 1. Characterization of the transferred CVD monolayer WSe₂. (a,b) The optical image of transferred CVD monolayer WSe₂ on SiO₂/Si substrate. (c) The AFM image at the edge of the monolayer film. (d) The height profile along the dotted red line in (c). (e,f) The typical Raman and photoluminescence spectra of the transferred film, respectively.

After the transfer and characterization of the WSe₂ monolayer, standard photolithography was applied to fabricate WSe₂ transistors. Figures S1a and S1b show the device structure and optical photograph of the phototransistor, where the 10/80nm Ti/Au or 10/80nm Pd/Au interdigitated electrodes are deposited by thermal evaporation, respectively, to form two types of metal-semiconductor-metal (MSM) structures: high Schottky-contact and low Schottky-contact based photodetector devices. All of the electrical and optical properties were measured at room temperature.

We first present the electrical transport properties of the CVD monolayer WSe₂ transistor with Pd metal contacts, where the work function of Pd is much higher than that of the WSe₂ monolayer.²⁴ As depicted in the back-gate transfer characteristics in Figures 2a and 2b, the Pd-contacted transistor exhibits obvious *p*-type conduction, and the threshold voltage is ~0V in ambient air. The unipolar *p*-type behavior of the Pd-contacted photodetector suggests that the

Fermi level is aligned close to the valence band of the monolayer WSe₂.^{24,33-35} The maximum transconductance is $g_m = dI_d/dV_g = 84.9 \mu S$ at $V_{ds} = 2V$ in the measurement gate voltage range, and the subthreshold swing is $S = dV_g/d(\log I_d) = 283 mV/decade$ in our bottom gate structure. According to the standard model of metal-oxide-semiconductor field effect transistors and the parallel plate model of gate capacitance, the hole mobility $\mu = g_m L / (WC_{ox} V_{ds})$ is $\sim 7.3 \text{ cm}^2/Vs$ in ambient air, where L is the channel length, W is the channel width, V_{ds} is the drain voltage, and C_{ox} the capacitance of the 300nm SiO₂. The ON/OFF current ratio of the Pd-contacted transistor is up to an impressive value of $\sim 10^9$, and the dark current is $\sim 10^{-12} A$ in the OFF state.

Figure 2. Optoelectrical properties of the CVD monolayer WSe₂ phototransistor in ambient and vacuum with Pd metal contacts. (a,b) I_d - V_g transfer characteristics of the transistor on a logarithmic and linear scale, respectively, in dark and at the laser power density 3.8 W/m², 0.22 W/cm² and $V_{ds} = 2V$. The measured conditions are: dark in ambient (black solid), 3.8 W/m² light in ambient (red solid), 0.22 W/cm² light in ambient (blue solid), dark in vacuum (dark cyan short dash), and 0.22 W/cm² light in vacuum (magenta short dash). (c) I_d - V_{ds} characteristics of the transistor as a function of light intensity on a logarithmic scale, at $V_g = 0V$. From bottom to top, the curves are measured at the following intensities: in

dark (black), 3.8W/m² (red), 59.5W/m² (blue), 595.3W/m² (dark cyan) and 0.22W/cm² (magenta). (d) The power dependence of the photocurrent at V_g=8V (OFF-state) and V_g=-60V(ON-state).

To evaluate the performance of the photodetector, the light power density (P₀) dependence of the photocurrent is studied with a continuous wavelength 650nm laser illumination in ambient air with spot size of ~1mm. The high sensitivity of the photodetector can be seen in Figure 2c, where the current is reversibly varied between 1 to 4 orders of magnitude by changing the light intensity from 3.8W/m² to 0.22W/cm². As shown in Figure 2d, the photocurrent ($I_{ph} = I_{illumination} - I_{dark}$) increases almost linearly with light power density ($I_{ph} \sim P_0^{0.91}$) in the OFF state at V_g=8V, V_{ds}=2V, demonstrating the efficiency of electron-hole pair generations is almost proportional to the absorbed photon flux.¹² However, the photocurrent becomes significantly sublinear with light power density in the ON state (at V_g=-60V, V_{ds}=2V; red curve in Figure 2d), indicating that the recombination of photoexcited electron-hole pairs becomes pronounced, or a different photocurrent-generated mechanism occurs in the ON state.^{12,18, 36,37} To quantitatively define the performance of the photodetector, we extract the photo responsivity and photo gain of the device (Figures 3a and 3b). For the OFF state (V_g=8V, V_{ds}=2V and P₀=3.8W/m²) in ambient, the photo responsivity $R=I_{ph}/P$ is ~ 0.008 A/W, where P is the absorbed laser power, and the photo gain $G=Rh\nu/\eta q$ is ~0.016 assuming that $\eta=100\%$, where h is the Planck constant, ν is the frequency of the incident laser, η is the external quantum efficiency, and q is the electron charge.³⁸ Interestingly, the photo responsivity and gain of the photodetector in ambient drastically increase to ~1.8×10⁵ A/W, and 3.5×10⁵, respectively, in the ON state(V_g=-60V, V_{ds}=2V and P₀=3.8W/m²). The values of photo responsivity and gain obtained are much higher than those of commercial silicon and InGaAs photodetectors.^{13,39-41} Specific detectivity is another figure of merit for photodetectors, which is related to the sensitivity that a detector can distinguish from the

background noise. The shot noise from the dark current is assumed to be the major contributor to the total noise and the specific detectivity given by $D^* = RA^{1/2}/(2qI_d)^{1/2}$,¹³ where R is the photoresponsivity, A is the area of the detector, q is the unit of charge, and I_d is the dark current. As shown in Figure 3c, D^* in the ON state is higher than 10^{14} Jones in ambient air at $V_g = -60V$, $V_{ds} = 2V$ and $P_0 = 3.8W/m^2$. The value is higher than that of commercial silicon ($\sim 10^{13}$ Jones) or InGaAs (10^{12} - 10^{13} Jones) photodetectors.^{13,39-41} Even for the ON state at a high power density of $P_0 = 0.22W/cm^2$ in ambient, D^* is still $> 10^{12}$ Jones, which is comparable to commercial silicon and InGaAs photodetectors. In the OFF state at $V_g = 8V$ and $V_{ds} = 2V$, the photodetector exhibits stable and good specific detectivity around 10^{11} - 10^{12} Jones with light power density from $3.8W/m^2$ to $0.22W/cm^2$. The different photoresponse behaviors in ON and OFF states suggest that various mechanisms are at work.^{12,18,36,37}

We have also studied the photoresponse properties of the WSe₂ monolayer phototransistor in high vacuum. As shown in Figure 2a, after vacuum pumping to 3.5×10^{-5} mbarr, the p-channel threshold voltage of the device shifts from 0 to -27V, and the n-channel begins to conduct. The device becomes ambipolar, which means that the ambient adsorbates withdraw electrons from WSe₂, resulting in apparent p-doping of the WSe₂ monolayer device.¹² The Fermi level of WSe₂ moves from close to the valence band to nearer the midgap; thus, the Schottky barrier at the interface between the metallic electrodes and WSe₂ monolayer is higher in vacuum than in ambient. When illuminating with the CW 650nm laser at $P_0 = 0.22W/cm^2$ and $V_{ds} = 2V$, the current in the OFF state increases more than 3 orders of magnitude (Figure 2a and 2b); however, the accumulation current in the ON state does not increase with the incident light, in sharp contrast to that in ambient air. Figures 3d to 3e compare the performance of the phototransistor in ambient and high vacuum, and it can be seen that the photo gain and specific detectivity in the

OFF states are almost the same, while both the photo gain and specific detectivity in the ON states decrease by more than 3 orders of magnitude from ambient to high vacuum. It has been suggested that, in the OFF state, the Schottky barrier is so high that the thermionic and tunneling currents are negligible, and the photogenerated current is the dominant channel current under illumination.^{13,14,18} In the ON state, the movement of the Fermi level and the bending of energy band by the applied gate electric field result in the Schottky barrier height decrease; hence in this case the thermionic and tunneling currents dominate the channel current. For the Pd-contacted WSe₂ phototransistor in the ON state (cf. Figures 2a and 2b), the photogenerated current is negligible in high vacuum. In contrast, the photogenerated current is very high in ambient, resulting in high photo gain and specific detectivity. These different photoresponse properties are attributed to the desorption of adsorbates in ambient air, causing the Fermi level of the WSe₂ monolayer to move towards the minimum of the conduction band and increase the Schottky barrier height at the electrode/WSe₂ interface.^{42,43}

Figure 3. Performance of the phototransistor based on CVD WSe₂ monolayer with Pd metal contacts. (a,b,c) The light power density dependence of the photo responsivity, photo gain, and specific detectivity, respectively. (d,e) The photo gain and specific detectivity of the photodetector in ambient air and vacuum at laser power density 0.22W/cm² and V_{ds}=2V. (f) The time-resolved photoresponse of the device in ambient (black) and vacuum (red) at V_{ds}=2V, V_g=0V, P₀=170W/m².

To verify that the Schottky barrier plays an important role, we fabricate monolayer WSe₂ photodetectors contacted with Ti, whose work function is close to that of WSe₂.²⁴ Figures 4 and S2 present the electrical and photoresponse properties of the device. In Figure 4a, the Ti-contacted phototransistor exhibits ambipolar behavior in ambient, and the threshold voltages in p and n channels are -2 and 8V, respectively, indicating that the Fermi level of the WSe₂ monolayer is close to the midgap, and the Schottky barrier in the p channel is much higher than that with Pd

metal contacts.³³⁻³⁵ In high vacuum, the threshold voltages shift to negative voltages, consistent with the Pd-contacted device. The Fermi level moves to the minimum of the conduction band, resulting in an increase of the Schottky barrier in the p channel. As expected, with the increase of the Schottky barrier for the Ti-contacted WSe₂ photodetector in ambient, the channel current in the ON state does not change significantly under illumination (Figures 4a and 4b), similar to that for the Pd-contacted device in high vacuum, when the Fermi level is near the midgap. There is almost no photocurrent in the ON state for the Ti-contacted WSe₂ photodetector in ambient, which confirms that the increase of the Schottky barrier in the p channel results in the performance degradation of WSe₂ photodetection.

Figure 4. Room temperature photoresponse of the CVD monolayer WSe₂ phototransistor with Ti metal contacts. (a,b) I_d - V_g transfer characteristics of the photodetector on a logarithmic and linear scale, respectively, in dark and at the laser power density $0.4 W/cm^2$, $V_{ds}=2V$. The measured conditions are: dark in ambient (black solid), light in ambient (red solid), dark in vacuum (blue short dash), and light in vacuum (dark cyan short dash). (c) The laser power dependence of the photocurrent at $V_{ds}=2V$ and $V_g=0V$.

(d) The time-resolved photoresponse of the device in ambient (black) and vacuum (red) at $V_{ds}=2V$, $V_g=0V$, $P_0=0.4W/cm^2$.

Normally, the Schottky barrier at the metal/semiconductor interface plays a crucial role in determining the optoelectronic transport property of the MSM structure.⁴⁴ At a fixed bias voltage, the voltage drop occurs mainly at the reverse biased Schottky barrier for the Schottky contact photodetector.⁴⁵⁻⁴⁸ The photogenerated electron-hole pairs in the depletion region are separated by the strong local electric field, thus reducing the electron-hole recombination rates and increasing the free carrier density. Theory and experiments have shown that in the depletion region at the interface between the metallic electrodes and the low dimensional material, the potential tail decays extremely slowly, and the depletion region due the Schottky barrier can extend to several μm in the channel.^{46,49} Once the Schottky barrier decreases, the width of the barrier decreases.⁴⁶ The depletion region with the ohmic-like contact can be narrow enough such that the voltage drop associated with adsorbates, defects or charge impurities becomes important.^{46,48} Alternatively, the photothermoelectric effect may dominate the photocurrent.¹⁸ As shown in Figure 5a, the Fermi level of the CVD WSe₂ monolayer is near the valence band after contacting with Pd metal electrodes. In the OFF state(Figure 5c), the Fermi level is near the midgap, and the Schottky barrier is so high that the depletion region can extend several μm into the WSe₂ monolayer channel due to the larger band gap of monolayer WSe₂ and the $\sim 10\mu m$ channel length.^{46,49} Thus, the long depletion region with high voltage drop can efficiently separate the photogenerated electron-hole pairs, resulting in the linear power dependence of the photocurrent and fast response time (Figures 3f, 4c and 4d).⁵⁰ In the ON state with the Pd-contacts (Figure 5e), the Fermi level is near the valence band, and the Schottky barrier is so small that the depletion width becomes very narrow,⁴⁶ and the photogenerated carriers in the

depletion region could be negligible.^{13,14} However, the voltage drop from adsorbates, defects or charge impurities in the channel become prominent.^{46,48} Thus, photodesorption or photoexcitation through defect or charge impurity states to band edge may contribute to photocurrents in the ON state (Figure 2a),^{42,46,51} or the photothermoelectric effect could generate the photocurrent for the majority carriers (holes) of the WSe₂ could easily diffuse into the electrodes to produce the photocurrent.^{18,52} As shown in Figure 3f, the photocurrent for the Pd-contacted photodetector in ambient air takes more than 5s to saturate, and the response time can be resolved into two parts: fast response of less than 50ms, and slow response of longer than 5s. We attribute the fast response component to band-to-band excitation, and the slow response time to the desorption or excitation through defect or charge impurity states to the band edge,^{12,42} or to the photothermoelectric effect.^{18,52}

Figure 5. Energy band diagram of the photodetector based on the CVD WSe₂ monolayer. (a), (c) and (e) The band diagram of the device with Pd metal contacts in the equilibrium, OFF and ON state for hole carriers in the channel, respectively. (b), (d) and (f) The band diagram with Ti metal contacts in the equilibrium, OFF and ON state for hole carriers in the channel, respectively. E_F is the Fermi level energy, E_C is the minimum conduction band energy, E_V is the maximum valence band energy, and Φ_B is the Schottky barrier. In the (e), I_{TE} indicates the photocurrent from the photo thermoelectric effect, T_e is the electron trapping state near to the minimum conduction band edge, and T_h is the hole trapping state near to the maximum valence band edge. W_S and W_D are the depletion regions at the source electrode/WSe₂ and drain electrode/WSe₂ interfaces, respectively. S and D indicate the source and drain electrodes, respectively. The source electrode is grounded and the drain electrode is applied with a positive voltage in the experiment.

As the work function of Ti is close to that of the WSe₂ monolayer, the Fermi level alignment is

near the midgap of WSe₂ after contacts are made (Figure 5b).³³⁻³⁵ Thus, the Schottky barrier is much higher than that with Pd metal contacts. In the OFF state for the Ti-contacted transistors, as shown in Figure 5d, there are two depletion regions W_S and W_D , which are from the high Schottky barrier between the source/drain electrodes and the channel,^{46,53} and the process of generating a photocurrent with the Ti metal contacts is almost the same as that with the Pd metal contacts. However, in the ON state, in order to bend the energy band for the high Schottky barrier, the applied gate voltages are so high that the energy band near the drain electrode is also bent upwards, and two depletion regions are formed (Figure 5f),^{46,53} one near the source electrode (W_S) and the other near the drain electrode (W_D). As shown in Figure 5f, the photocurrents from the two depletion regions almost disappear owing to the two opposite regions connecting, and the two depletion regions make the voltage drops of the adsorbates, defects or charge impurities in the channel negligible. The photothermoelectric effect could not generate the photocurrent for the high Schottky barrier blocking the holes in WSe₂ to diffuse into the electrodes. Hence, the thermionic and tunneling currents dominate the channel current. As shown in Figure 4, the hole electric field mobility of the Ti-contacted WSe₂ photodetector decreases to 2.43 cm²/Vs, and the subthreshold swing for the p channel decreases to 320mV/decade. Compared with the Pd-contacted photodetector, the photo gain and specific detectivity of the Ti-contacted photodetector decreases under the same experimental conditions (Figures S2c and S2d). The decrease in the mobility, subthreshold swing, photo gain and specific detectivity is attributed to the increase of the Schottky barrier height. However, the laser power dependence of the photocurrent becomes more linear, where $I_{ph} \sim P^{0.95}$, and only the fast part of the response time for the Ti-contacted photodetector in the ambient air is observed, which means that photothermoelectric generated photocurrents, photocurrents due to desorption or excitation

through defect/charge impurity states to the band edge are not dominating factors. Interestingly, the response time of the Ti-contacted device remains less than 23ms after one month in ambient air (Figures 6a and 6b), while the response time of the Pd-contacted device becomes much longer, which could be due to the movement of Fermi level further towards the valence band and the decrease of Schottky barrier height. In the supporting materials (Figure S3), we present another typical Ti-contacted device which retains its performance even after aging for half a year.

Figure 6. (a) Photoswitching behaviors of the Pd- and Ti-contacted photodetectors aged in ambient for one month. (b) Photoswitching rate of the photodetector with Ti metal contacts in ambient. The laser power density is 863W/m^2 , $V_{ds}=2\text{V}$ and $V_g=0\text{V}$. (c) The wavelength dependence of the photo responsivity for the CVD monolayer WSe_2 photodetector at $V_{ds}=2\text{V}$, $V_g=0\text{V}$. (d) The absorbance spectrum of a CVD monolayer WSe_2 .

The wavelength dependence of the photocurrent for the Ti-contacted WSe_2 phototransistor is shown in Figure 6c. The phototransistor exhibits good wavelength selectivity. When the light wavelength is shorter than 800nm, the responsivity is $\sim 10^{-4}\text{A/W}$ in the OFF state. It increases to

0.032 A/W and 0.171 A/W under the 750nm and 550nm wavelength illumination, respectively. The profile of the wavelength dependence of the responsivity is consistent with the absorption spectrum (Figure 6d), indicating that the generated photocurrent is from the WSe₂ monolayer.

CONCLUSIONS

In conclusion, CVD monolayer WSe₂ phototransistors have been fabricated, and the Schottky contact effect on their optoelectronic properties has been investigated in detail. We propose a qualitative mechanism based on energy band bending at the metal/semiconductor junction to explain our observations. The phototransistor with Ti metal contacts exhibits fast photoresponse, where the rise and decay times are shorter than our detection limit, i.e. 23ms. Furthermore, the high performance remains stable even after half a year in ambient. These phototransistors based on the CVD WSe₂ monolayer are significantly better than that of CVD monolayer MoS₂ in terms of response time and material/device stability in ambient. With its high photo gain, high detectivity, fast response speed, and high stability, the CVD monolayer WSe₂ phototransistors are demonstrated to display significant potential for future optoelectronic applications.

METHODS

Growth of monolayer WSe₂: The WO₃ powders (0.3 g) were placed in a ceramic boat located in the heating zone center of the furnace. The Se powders were placed in a separate ceramic boat at the upper stream side maintained at 270°C during the reaction. The sapphire substrates for growing WSe₂ were put at the downstream side, where the Se and WO₃ vapors were brought to the targeting sapphire substrates by an Ar/H₂ flowing gas (Ar = 80 sccm, H₂ = 20 sccm, chamber pressure = 1 Torr). The center heating zone was heated to 925°C at a ramping rate of 25 C/min. Note that the temperature of the sapphire substrates was at ~750 to 850°C when the center heating zone reaches 925°C. After reaching 925°C, the heating zone was kept for 15 min and the furnace was then naturally cooled to room temperature.

Transfer process: An as-grown WSe₂ film was spin-coated by a layer of polymethyl methacrylate (PMMA), and baked at 100°C for 1 hour. Then, the PMMA-coated WSe₂ film was put into 2M NaOH solution at 100°C for 1 hour, and subsequently the PMMA-supported WSe₂ film was detached from sapphire substrate and floated on the surface of NaOH solution. Then, the floating PMMA-supported WSe₂ film was transferred to deionized (DI) water to remove the residual etchant. Using SiO₂/Si substrate to fish up the PMMA-coated WSe₂ film, and followed with 100°C drying for 30 min. Finally, the PMMA was removed by acetone, isopropyl alcohol (IPA) and DI water rinsing.

Device Fabrication: The phototransistors were fabricated by direction deposition of contact metals on desired 2D layers using a hardmask to define the metal area, where the 10/80nm Ti/Au or 10/80nm Pd/Au interdigitated electrodes are deposited by thermal evaporation, respectively, to form two types of metal-semiconductor-metal (MSM) structures. The as-fabricated devices were directly sent for electrical measurements without performing any thermal annealing. .

Characterizations: The AFM images were obtained using a Veeco Dimension-Icon system. Raman and PL spectra were collected in a confocal Raman/PL system (NT-MDT). The wavelength of the laser was 473 nm (2.63 eV), and the spot size of the laser beam was ~0.5 μm. The spectral resolution was 3 cm⁻¹ (obtained with a 600 grooves mm⁻¹ grating). A high grating (1800 grooves mm⁻¹) was also used to obtain more details of the line shapes of the Raman band, and the spectral resolution was 1 cm⁻¹. The Si peak at 520 cm⁻¹ was used as a reference for wavenumber calibration, and the peak frequency was extracted by fitting a Raman peak with a Lorentz function. The electrical measurements were performed under ambient or vacuum conditions using a Keithley semiconductor parameter analyzer, model 4200-SCS. A 650 nm laser was used to measure the photoresponse of the devices, and the spot size was ~1 mm.

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