Optoelectronic devices based on electrically tunable p–n diodes in a monolayer dichalcogenide

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The ideality factor of the nV is the Lambert bias current and will be a focus of future work. The roll-off of contributions from Shockley–Read–Hall or Auger processes, will strongly rectify current in opposite directions.

The rapid increase in current under forward bias defines an advantage of a lateral device geometry. Although our data do not strongly constrain the value of \( I_{bg} \), because it is below the 1 pA noise floor of the measurement, uncertainty in \( I_{bg} \) has an insignificant effect on the fits to the slope and roll-off of the current, and does not impact the values of \( n \) and \( R_s \). Both diodes have rectification factors of \( 10^5 \) and reverse bias currents of \( <1 \) pA up to \( |V_{ds}| = 1 \) V, representing promising characteristics for low-power electronics.

A more complete view of transport through the device is shown in a map of current as a function of \( V_{bg} \) and \( V_{fg} \) (Fig. 2). The four corners of the map show the extremes of the four doping configurations (NN, PP, PN and NP). The off state of the device can be seen in the dark blue region in the centre of the map, separating the four conducting regions. Although mid-gap states, most likely due to disorder, form a conducting region between the NN and NP quadrants, current through these states is thermally activated and can be eliminated by cooling the device (Supplementary Fig. 3).

Along the diagonal line defined by \( V_{bg} = V_{fg} = V_{bg} \), line cuts show the device operating as an ambipolar field-effect transistor with a series resistance, \( R_s \):

\[
I_{ds} = \frac{nV_T}{R_s} W \left[ \frac{I_0 R_s}{nV_T} \exp \left( \frac{V_{ds} + I_0 R_s}{nV_T} \right) \right] - I_0
\]

with \( V_T = k_BT/q \) the thermal voltage at temperature \( T \), \( k_B \) the Boltzmann constant, and \( q \) the electron charge. \( I_0 \) is the reverse-bias current and \( n \) is the diode ideality factor (\( n = 1 \) is ideal). \( W \) is the Lambert \( W \) function.

The increase in current at high reverse bias indicates a high-quality p–n interface and an expected advantage of a lateral device geometry. Although our data do not strongly constrain the value of \( I_{bg} \), because it is below the 1 pA noise floor of the measurement, uncertainty in \( I_{bg} \) has an insignificant effect on the fits to the slope and roll-off of the current, and does not impact the values of \( n \) and \( R_s \). Both diodes have rectification factors of \( 10^5 \) and reverse bias currents of \( <1 \) pA up to \( |V_{ds}| = 1 \) V, representing promising characteristics for low-power electronics.

Figure 1 | Gate-controlled monolayer WSe₂ p–n junction diodes. a. Top: Optical micrograph of a monolayer WSe₂ device controlled by two local gates. The WSe₂ is contacted with gold electrodes. The flake and contacts are insulated from the gates by 20 nm HfO₂. Scale bar, 2 µm. Bottom: schematic side view of the device including electrical connections. 

b. Current-voltage (\( I_{ds}-V_{ds} \)) curves showing transport characteristics of four doping configurations of the device: NN, PP, PN and NP. Both gates were set to 10 V for the NN configuration and -10 V for PP. \( V_{bg} \) was set to ±10 V and \( V_{fg} \) to ±1 V for PN/NP. The NN and PP configurations (yellow and black curves, respectively) are ohmic at low \( V_{ds} \), while the PN and NP configurations (blue and green curves, respectively) strongly rectify current in opposite directions. 

c. Semi-logarithmic plots of \( I_{ds} \) through the PN (blue circles) and NP (green circles) diodes as a function of \( V_{ds} \), with fits in yellow (see text). The fits give a diode ideality of \( n = 1.9 \) for both the PN and NP configurations. Insets: Schematic band diagrams of the device in forward bias for PN and NP configurations.
Scanning the beam (power 75 µW, wavelength 830 nm) over the sample and measuring \( I_{ds} \) at \( V_{ds} = 0 \) yields a spatial map of the photoresponse of the device (Fig. 3b). Calibrating the photocurrent map with a simultaneously acquired image of reflected light from the sample (Supplementary Fig. 4), we overlaid the positions of the contacts and gates to demonstrate that maximum photocurrent arises when light is incident on the junction. A line cut through the centre of the photocurrent map is shown in Fig. 3c with the positions of the contacts and the junction illustrated for reference. The photocurrent is symmetric and centred on the junction, demonstrating that the photoresponse is dominated by the p–n junction and not Schottky barriers at the contacts (Supplementary Fig. 3).

At relatively large \( V_{ds} \) in the NP configuration, a substantial photocurrent is generated when the junction is illuminated with laser light at 532 nm. The \( I_{ph} \)–\( V_{ds} \) curves at laser powers of 0–10 µW are shown in Fig. 3d. The photocurrent \( I_{ph} = I_{ds, light} - I_{ds, dark} \) at \( V_{ds} = -2 \) V and a linear fit of \( I_{ph} \) up to 8 µW are shown in the inset. The slope from the fit gives a responsivity of 210 mA W\(^{-1}\), which is comparable to commercial silicon photodetectors for green light. We note that phototransistors based on monolayer dichalcogenides can achieve even higher responsivities\(^{16}\), although the principle of operation and device geometry differ significantly from the photodiodes presented here.

In addition to photodetection, monolayer WSe\(_2\) p–n diodes are also capable of photovoltaic power generation. With the device in the NP configuration, current is measured as a function of \( V_{ds} \) for various laser powers from a supercontinuum white-light source bandpass filtered at 700 nm. Figure 4a presents a zoomed-in view of the \( I_{ph} \)–\( V_{ds} \) curve, focusing on the quadrant of photovoltaic power generation. The short-circuit current \( I_{sc} \), which is the zero-bias current through the illuminated device, increases linearly with power up to at least 10 µW (Fig. 4a, inset). The power generated by the photovoltaic device, \( P = I_{ph} V_{ds} \), is shown for laser...
The external quantum efficiency, EQE, quantifies the efficiency of light conversion into current, we extract the effect in these WSe₂ diodes is approximately an order of magnitude larger than photothermoelectric currents observed at the contacts of the p–n junction relative to the size of the laser spot, which together suggest an internal quantum efficiency at least an order of magnitude larger than the EQE reported here.

Finally, we measure the electroluminescence spectrum of a second monolayer WSe₂, p–n diode (Fig. 4d). To improve hole injection, this device was fabricated with palladium instead of gold to contact the p-type WSe₂ (Supplementary Fig. 2). In the PN configuration (Vₐ₈ = 2 V, Iₘ₈ = 100 nA), the device behaves as a light-emitting diode. The emitted light spectrum peaks at 752 nm, corresponding to the direct-gap exciton transition seen in the photocurrent spectrum (Fig. 4d). Using a blackbody source for calibration, we estimate the electroluminescence efficiency, defined as optical output power divided by electrical input power, to be ~1%. Light emission and a peak at ~750 nm are also seen in the NP configuration (Vₐ₈ = 2 V, Iₘ₈ = 4 nA), with a peak height smaller in powers of 0–10 μW in Fig. 4b. The photovoltaic power generation also has a linear dependence on laser power (Supplementary Fig. 5).

Varying Vₐ, the asymmetric gate voltage that defines the junction, at different laser powers, we observe a saturation in the short-circuit current when Vₐ ≈ ±5 V (Fig. 4c). The current is higher for NP than for PN due to a difference in contact resistances between the two contacts. We also note that the photocurrent due to the photovoltaic effect in these WSe₂ diodes is approximately an order of magnitude larger than photothermoelectric currents observed at the contacts of a monolayer MoS₂ field-effect transistor²⁹.

To obtain spectrally resolved photocurrent in the NP configuration, we measure Iₘ₈ as a function of excitation wavelength. To quantify the efficiency of light conversion into current, we extract the external quantum efficiency, EQE = (Iₘ₈/P₉₉₉₉λ)(hc/λ), as a function of wavelength λ, at constant laser power P₉₉₉₉, where h, c and e are Planck's constant, the speed of light and electron charge, respectively. We observe three peaks in the spectrally resolved photocurrent at 755, 591 and 522 nm (Fig. 4d), corresponding to energies of 1.64, 2.10 and 2.38 eV, respectively. These energies match well with the values observed via photoluminescence, differential reflectance¹⁹ and optical absorption spectroscopy²⁰ for the A, B and A' transitions of monolayer WSe₂, as depicted in the band diagram in the inset to Fig. 4d. We measure a maximum EQE of 0.2% at 522 nm. This value does not take into account the low absorption of monolayer WSe₂ on the narrow cross-section of the p–n junction relative to the size of the laser spot, which together suggest an internal quantum efficiency at least an order of magnitude larger than the EQE reported here.

Finally, we measure the electroluminescence spectrum of a second monolayer WSe₂, p–n diode (Fig. 4d). To improve hole injection, this device was fabricated with palladium instead of gold to contact the p-type WSe₂ (Supplementary Fig. 2). In the PN configuration (Vₐ₈ = 2 V, Iₘ₈ = 100 nA), the device behaves as a light-emitting diode. The emitted light spectrum peaks at 752 nm, corresponding to the direct-gap exciton transition seen in the photocurrent spectrum (Fig. 4d). Using a blackbody source for calibration, we estimate the electroluminescence efficiency, defined as optical output power divided by electrical input power, to be ~1%. Light emission and a peak at ~750 nm are also seen in the NP configuration (Vₐ₈ = 2 V, Iₘ₈ = 4 nA), with a peak height smaller in
proportion to \( I_{ds} \). No emission is seen in either NN (with \( V_{ds} = 2 \) V and \( I_{ds} = 300 \) nA) or PP (with \( V_{ds} = 2 \) V and \( I_{ds} = 500 \) nA) configurations, confirming that the gate-defined p–n junction generates the electroluminescence. A spatial image of light emission from a third device is shown in Supplementary Fig. 6.

Based on the device performance presented here, we anticipate a prominent role for diodes and optoelectronic devices based on monolayer dichalcogenide p–n junctions. Taking into account the three-atom thickness and low optical absorption of monolayer WSe\(_2\) (ref. 30), the responsivity and EQE reported here are quite substantial. Furthermore, the device geometry could be optimized to significantly enhance the photoresponse. We expect that vertical junctions based on transfer-aligned exfoliated flakes\(^{25}\) or large-area dichalcogenides grown by chemical vapour deposition\(^{30}\) could increase responsivity and EQE by more than an order of magnitude. Additionally, improved contact resistance, particularly for holes, should dramatically improve device performance.

In conclusion, we have demonstrated electrically tunable p–n diodes based solely on monolayer WSe\(_2\). These diodes strongly rectify current, in a direction selectable by the two gates controlling the device. Both PN and NP configurations have diode ideality factors of \( n = 1.9 \) and a rectification factor of \( 10^5 \). With laser light incident on the junction, these diodes produce a large photocurrent with a responsivity of 210 mA W\(^{-1}\) at high bias. At low bias, the diodes generate power via the photovoltaic effect, with a peak EQE of 0.2% at 522 nm. The spectral response of the photocurrent from visible to near-infrared wavelengths showed peaks corresponding to the three lowest excitonic transitions expected for monolayer WSe\(_2\).

Finally, these devices also function as light-emitting diodes with an electroluminescence peak at 752 nm. These p–n diodes demonstrate the potential of monolayer WSe\(_2\), in addition to other direct-gap semiconducting dichalcogenides, for novel electronic and optoelectronic applications. As device quality improves, they also lay the foundation for more fundamental quantum transport experiments\(^{31}\).

**Note added in proof**: During the preparation of this Letter we became aware of two similar studies\(^{32,33}\).

**Methods**

Device fabrication began with exfoliation of bulk, natural WSe\(_2\) (Nanosurf) down to few-layered sheets using the mechanical cleavage method pioneered for graphene. The thin flakes were deposited onto a transfer slide composed of a stack of glass, a polymer (polydimethylsiloxane, PDMS) and a resist (methyl methacrylate, MMA).
as described for graphene–boron nitride device fabrication. Single molecular layers were identified by optical contrast. Layer number was later confirmed using atomic force microscopy and either photocurrent spectroscopy or electroluminescence (Supplementary Section ‘Device Fabrication’). The monolayers were transferred onto a pair of split gates covered by 20 nm HfO2 (grown by atomic layer deposition at 80 °C). The gates were separated by a 100 nm gap, patterned using electron-beam lithography on a highly doped silicon substrate covered in 285 nm thermally grown SiO2. The gates were made from electron-beam evaporated gold and were 20 nm thick. The two backgates were capacitively coupled to the device through the HfO2 dielectric, which has a dielectric constant, \( \epsilon_r \approx 20 \). The WSe2 was contacted by two gold electrodes, each \( \sim 1 \mu m \) wide and 25 nm thick, with a 0.3 nm chromium sticking layer.

All measurements were performed at room temperature and in vacuum (\( \sim 10^{-3} \) torr) to avoid device degradation from adsorbates present in air, which could be mitigated by encapsulation of the WSe2. Electroluminescence was measured using a liquid nitrogen-cooled charged-coupled device with an integration time of 60 s. A background measured at \( V_d = 0 \) was subtracted from all four electroluminescence traces in Fig. 4d.

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References
1. Martel, R. et al. Ambipolar electrical transport in semiconducting single-wall carbon nanotubes. Phys. Rev. Lett. 87, 256805 (2001).
2. Koo, S.-M., Li, Q., Edelstein, M., Richter, C. & Vogel, E. Enhanced channel dielectric, which has a dielectric constant, \( \epsilon_r = 15 \). The WSe2 was contacted by two gold electrodes, each \( \sim 1 \mu m \) wide and 25 nm thick, with a 0.3 nm chromium sticking layer.
3. Zaumseil, J. & Sirringhaus, H. Electron and ambipolar transport in organic field-effect transistors. Chem. Rev. 107, 1296–1323 (2007).
4. Bertolazzi, S., Brivio, J. & Kis, A. Stretching and breaking of ultrathin MoS2. ACS Nano 5, 9703–9709 (2011).
5. Mak, K. F., Lee, C., Hone, J., Shan, J. & Heinz, T. F. Atomically thin MoS2: a new direct-gap semiconductor. Phys. Rev. Lett. 105, 136805 (2010).
6. Huang, J.-K. Near-ideal electrical properties of InAs/WSe2 van der Waals heterojunction diodes. Appl. Phys. Lett. 102, 242101 (2013).
7. Tomonord, P. et al. Photoluminescence emission and Raman response of monolayer MoS2, MoSe2, and WSe2, Opt. Express 21, 4908–4916 (2013).
8. Zhao, W. et al. Evolution of electronic structure in atomically thin sheets of WS2 and WSe2, ACS Nano 7, 791–797 (2013).
9. Geim, A. K. & Grigorieva, I. V. Van der Waals heterostructures. Nature 499, 419–425 (2013).
10. Wilson, J. & Yoffe, A. The transition metal dichalcogenides discourse and interpretation of the observed optical, electrical, and structural properties. Adv. Phys. 18, 193–335 (1969).
11. Podzorov, V., Gershenson, M. E., Kloč, C., Zeis, R. & Bucher, E. High-mobility field-effect transistors based on transition metal dichalcogenides. Appl. Phys. Lett. 84, 3301–3303 (2004).
12. Radisavljevic, B. & Kis, A. Mobility engineering and a metal–insulator transition in monolayer MoS2, Nature Mater. 12, 815–820 (2013).
13. Zhang, Y. J., Ye, J. T., Yomogida, Y., Takenobu, T. & Iwasa, Y. Formation of a stable p–n junction in a liquid-gated MoS2 ambipolar transistor. Nano Lett. 13, 3023–3028 (2013).
14. Wang, H. et al. Integrated circuits based on bilayer MoS2 transistors. Nano Lett. 12, 4674–4680 (2012).
15. Yin, Z. et al. Single-layer MoS2 phototransistors. ACS Nano 6, 74–80 (2012).
16. Lopez-Sanchez, O., Lembke, D., Kayci, M., Radenovic, A. & Kis, A. Ultrathin sensitive photodetectors based on monolayer MoS2. Nature Nanotech. 8, 497–501 (2013).
17. Sundaram, R. S. et al. Electroluminescence in single layer MoS2, Nano Lett. 13, 1416–1421 (2013).
18. Ye, Y. et al. Exciton-related electroluminescence from monolayer MoS2. Preprint at http://lanl.arXiv.org/abs/1305.4235 (2013).
19. Zeng, H. et al. Optical signature of symmetry variations and spin-valley coupling in atomically thin tungsten dichalcogenides. Sci. Rep. 3, 1608 (2013).
20. Mak, K. F., He, K., Shan, J. & Heinz, T. F. Control of valley polarization in monolayer MoS2. Nature Nanotech. 7, 494–498 (2012).
21. Sallen, G. et al. Robust optical emission polarization in MoS2 monolayers through selective valley excitation. Phys. Rev. B 86, 081301 (2012).
22. Jones, A. et al. Optical generation of excitonic valley coherence in monolayer WSe2. Nature Nanotech. 8, 634–638 (2013).
23. Spah, R., Elrod, U., Luxteinter, M., Bucher, E. & Wagner, S. PN junctions in tungsten diselenide. Appl. Phys. Lett. 43, 79–81 (1983).
24. Lee, J. U., Gipp, P. P. & Heller, C. M. Carbon nanotube p–n junction diodes. Appl. Phys. Lett. 85, 145–147 (2004).
25. Dean, C. R. et al. Boron nitride substrates for high-quality graphene electronics. Nature Nanotech. 5, 722–726 (2010).
26. Radisavljevic, B., Radenovic, A., Brivio, J., Giacometti, V. & Kis, A. Single-layer MoS2 transistors. Nature Nanotech. 6, 147–150 (2011).
27. Sah, C.-T., Noyce, R. N. & Shockley, W. Carrier generation and recombination in p–n junctions and p–n junction characteristics. Proc. IRE 45, 1228–1243 (1957).
28. Banwell, T. & Jayakumar, A. Exact analytical solution for current flow through diode with series resistance. Electron. Lett. 36, 291–292 (2000).
29. Buscema, M. et al. Large and tunable photo-thermoelectric effect in single-layer MoS2. Nano Lett. 13, 358–363 (2013).
30. Huang, J.-K. et al. Large-area and highly crystalline WSe2 monolayers: from synthesis to device applications. ACS Nano 8, 923–930 (2014).
31. Li, X., Zhang, F. & Niu, Q. Unconventional quantum Hall effect and tunable spin Hall effect in Dirac materials: application to an isolated MoS2 trilayer. Phys. Rev. Lett. 110, 066803 (2013).
32. Pospischil, A., Forch, M. M. & Mueller, T. Solar-energy conversion and light emission in an atomic monolayer p–n diode. Nature Nanotech. http://dx.doi.org/10.1038/nanotechnology.2014.14 (2014).
33. Ross, J. et al. Electrically tunable excitonic light-emitting diodes based on monolayer WSe2 p–n junctions. Nature Nanotech. http://dx.doi.org/10.1038/nanotechnology.2014.26 (2014).

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Author contributions
B.W.H.B., H.O.H.C. and Y.Y. fabricated the samples. B.W.H.B., H.O.H.C. and Y.Y. performed the measurements. All authors analysed the data and co-wrote the paper.

Additional information
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Competing financial interests
The authors declare no competing financial interests.