Environmentally Controlled Charge Carrier

Injection Mechanisms of Metal/WS$_2$ Junctions

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1 Methods

Clean surfaces are prepared by cleaving a bulk piece of muscovite mica in ambient conditions. WS$_2$ flakes are subsequently mechanically exfoliated on the mica substrate. The flakes are inspected for monolayers by optical microscopy and atomic force microscopy (AFM). The thin flakes are then electrically connected using graphite. The AFM tip is grounded and a voltage is applied to the sample. A schematic representation of the system is shown in Figure 1b in the main text. The samples and the AFM scanning head are inserted in a closed environmental chamber that can be purged with N$_2$ gas to control the relative humidity (RH). The RH of the environmental chamber is measured by a humidity sensor (SENSIRION EK-H4 SHTXX). This way the RH could be lowered to $< 1\%$ RH. To obtain ambient conditions, the nitrogen flow was stopped and the environmental chamber was opened, resulting in a RH of 40% - 60%.

The topography and conductive-AFM (c-AFM) measurements were obtained with an Agilent 5100 AFM. Topography and current images are recorded in contact mode with a conductive Pt tip (12Pt400B, Rocky Mountain Nanotechnology) with a nominal spring constant of 0.3 N/m and a tip radius smaller than 10 nm. Kelvin probe force microscopy (KPFM) maps are recorded with an Asylum Cypher AFM with a Pt probe using amplitude modulated lift mode. For the scanning tunneling microscope (STM) measurements an Omicron LT-STM is used in ultra high vacuum at room temperature with etched PtIr tips.

2 Layer thickness determination

To determine the thickness of the WS$_2$ flakes that we are measuring, we use AFM topography as shown in Figure S1a. In the figure, a single layer of WS$_2$ is shown on mica with a folded part. Because the surface forces of the AFM tip differ when scanning across a step of
one material to another (in our case: mica to WS$_2$), the height information is not straightforward to interpret. The step can appear much higher than would be expected or can even appear as a negative step, depending on the scanning parameters and trapped water layers and/or contamination layers.$^{1,2}$ Indeed a cross section across the two regions (mica and WS$_2$), shown in profile 2 in Figure S1b, shows a much higher step height than the single layer step height of 0.67 nm.$^1$ The measured step height is 3.5 nm, which is not uncommon for AFM measurements of 2D materials layer.$^{2,3}$ To accurately determine the layer thickness with AFM, one could make use of a cover layer such as graphene or a folded region, since in both cases tip interacts always with the same surface.$^{4,5}$ In our case we do not want to cover our sample. This is why we look for a folded piece to determine the thickness of our samples. We know that the folded piece has the same thickness as the surrounding flake and when scanning from the folded piece to the main flake, the tip experiences the same surface forces and thus the topography map only includes height information. The step height measured using this approach is shown in profile 1 in Figure S1b; 0.72 nm, close to the literature value of a single step (0.67 nm).$^1$ We also note here that the $z$ calibration of our AFM was done on a graphite sample using graphite’s well-known monoatomic step height. By knowing the height of the single-layer, we gradually move on to the thicker parts of the flake and accurately characterize its thickness as shown in Figures S1c and S1d. This way the thickness of the FL flake is determined to be 10 layers.
Figure S1: (a) Topography image showing a folded single-layer WS$_2$ flake. (b) Two line profiles corresponding to the profiles indicated in panel a. (c) Topography image showing the transition from the SL-WS$_2$ to the thicker part of the flake. (d) Line profile corresponding to the profile in panel c.

3 Thickness dependent work function

The contact potential difference is measured by KPFM for a flake of different thicknesses. As can be seen in the topography in Figure S2, the mica substrate is identified to the left of the scan while the WS$_2$ increases step-wise in thickness toward the right side of the scan as can be seen in Figure S2b. The contact potential difference map shown in Figure S2c was recorded simultaneously with the topography. Overall, the contact potential difference increases with layer thickness. This corresponds with a decreasing work function for thicker WS$_2$ as was found in other work.$^6$
Figure S2: (a) Topography map showing bare mica to the left of the image with a step-wise increase in WS₂ flake thickness toward the right of the image. (b) Cross section of the line profile indicated in panel a. (c) A contact potential difference map recorded simultaneously with the topography in a.

4 Contact potential difference KPFM areas

As can be seen in the KPFM map in Figure S3, there are variations in the measured contact potential difference ($V_{cpd}$) within the different regions: 2L-H₂O, 1L-H₂O and mica. The contact potential difference value assigned to each region is an average over a selected area in the map. The areas that are averaged to obtain this value are chosen with a threshold value. The resulting masks corresponding to these thresholds are shown in the left column where the top panel corresponds to the 2L-H₂O region, the middle panel to the 1L-H₂O region and the bottom panel to the bare mica. In the right column the corresponding distributions of $V_{cpd}$ is shown. The data obtained from the 2L-H₂O and mica regions have a normal distribution. The data obtained from the 1L-H₂O region has a clear trend, where $V_{cpd}$ is higher toward the edges of the ice fractals. This gradual tapering off of $V_{cpd}$ toward the center can be attributed either to horizontal charge screening or to artifacts due to tip-convolution.

The $V_{cpd}$ is directly related to the work function of the surface ($\Phi_{sample}$) by:


\[ V_{cpd} = \left( \phi_{\text{tip}} - \phi_{\text{sample}} \right)/e, \]

where \( \Phi_{\text{tip}} \) is the work function of the tip and \( e \) is the elementary charge. \( \Phi_{\text{tip}} \) is calibrated on a thick WS\(_2\) flake directly after the measurement on the thin flake. The measured \( V_{cpd} \) on the thick flake was 0.71 V. This can be related to the known work function of bulk WS\(_2\) of 4.3 eV,\(^6\) resulting in \( \Phi_{\text{tip}} = 5.0 \) eV.
Figure S3: The left column shows the contact potential difference maps of the three regions: 2L-H$_2$O, 1L-H$_2$O and bare mica. The mask that is used to differentiate between the different regions is indicated as a transparent red in each map. The right column shows the distribution of $V_{cpd}$ corresponding to the three maps.
5 STM data

$I(V)$ curves recorded with the STM show a gradual transition from the 2L-H$_2$O to the 1L-H$_2$O region as shown in Figures S4a-b. The color of the $I(V)$ traces in Figure S4b indicates the position with respect to the transition region as indicated in Figure S4a. $dI/dV$ curves are obtained by numerical differentiation of the $I(V)$ traces. A map of these $dI/dV$ curves is shown in the main manuscript in Figure 2f. The curves are recorded by first stabilizing the tip at -1 V, which is the reason that the $I(V)$ curves overlap at the negative bias. In Figure S4c, the $dI/dV$ curves recorded on 2L-H$_2$O and 1L-H$_2$O regions are compared. The $dI/dV$ data are proportional to the local density of states (LDOS). Because WS$_2$ is a semiconductor, there are only few states expected inside the band gap of 2.1 eV. From the recorded data it is difficult to determine the band edges. Still, some features are discernible in both curves and their shift in energy from 2L-H$_2$O to 1L-H$_2$O can be measured. Especially the small increase in LDOS at around -0.2 V is a good marker to trace the shift in work function. A smaller range image around this point is shown in the main manuscript in Figure 2e. Similar results have been obtained on fractals with a different shape such as the fractal in Figure S5a. A large range $dI/dV$ curve measured on this fractal is shown in Figure S5b.

Figure S4: (a) Cross section of an $I(V)$ grid map at 1 V. 2L-H$_2$O and 1L-H$_2$O regions are indicated. (b) $I(V)$ traces recorded over a transition region. The positions of the curves with respect to the transition are indicated by the respective colors in the grid map in panel a. (c) $dI/dV$ curves are obtained from $I(V)$ traces recorded on 2L-H$_2$O and 1L-H$_2$O regions over a bias range from -1 V to 1 V.
Figure S5: (a) Topography of a fractal ($V = -1.5$ V; $I = 200$ pA). (b) Large range $dI/dV$ trace recorded on the fractal of panel a.

6 Acquisition of the $I(V)$ curves

The $I(V)$ curves that are shown in the main text are obtained by averaging over multiple curves. The $I(V)$ curves are all obtained from an $I(V)$ grid. In the $I(V)$ grid, an $I(V)$ curve is taken at locations in a square grid of 256x256 equally spaced positions. For each $I(V)$ curve the piezo scanner is paused and the bias is ramped from -10 V to +10 V. Before the grid is recorded, a topography map is measured. This allows us to relate the $I(V)$ curves to a specific topographic location. In Figure S6 the topography maps and corresponding cross sections of the $I(V)$ grids are shown that have been used to produce the graphs in Figure 4 in the main text. Such a cross section of an $I(V)$ grid results in a current map. The topography map is shown in the left column, while a cross section of the corresponding $I(V)$ grid is shown in the right column. The curves are averaged over; 1030 curves (SL/2L-H$_2$O), 402 curves (SL/1L-H$_2$O), 3449 curves (BL/2L-H$_2$O), 558 curves (BL/1L-H$_2$O), 219 curves (FL/2L-H$_2$O), 644 curves (FL/1L-H$_2$O), 1889 curves (ML/2L-H$_2$O) and 4098 curves (ML/1L-H$_2$O).
Figure S6: (a) The topography of the $I(V)$ grid map where the $I(V)$ curves were extracted for thicknesses: SL, BL and FL. (b) A cross section of the grid $I(V)$ recorded at the same location as in a. Darker contrast indicates a higher current. The areas which were selected to extract the $I(V)$ curves: SL/1L-H$_2$O (purple), SL/2L-H$_2$O (yellow), BL/1L-H$_2$O (red), BL/2L-H$_2$O (blue), FL/1L-H$_2$O (green), FL/2L-H$_2$O (light-blue). (c) The topography of the $I(V)$ grid map where the $I(V)$ curves were extracted for the ML flake. (d) A cross section of the grid $I(V)$ recorded at the same location as c. The $I(V)$ curves used for the ML/1L-H$_2$O data are indicated in blue. The $I(V)$ curves used for the ML/2L-H$_2$O data are indicated in red.

7 Carrier injection mechanisms

By assuming the thermionic emission (TE), Fowler-Nordheim tunneling (F-N) and direct tunneling (DT) models on the measured data it is possible to acquire information about the
Schottky barrier. For TE, the Schottky barrier height ($\Phi_B$) and the ideality factor ($n$) can be acquired. As already mentioned in the main text, the thermionic emission model used for a metal/2D semiconductor contact is:\textsuperscript{8-11}

$$I = I_0 \exp \left( \frac{qV}{nk_BT} \right) \left[ 1 - \exp \left( -\frac{qV}{k_BT} \right) \right],$$  \hspace{1cm} (2)

$$I_0 = AA^* T^2 \exp \left( -\frac{q\Phi_B}{k_BT} \right).$$  \hspace{1cm} (3)

For $qV > k_BT$, this simplifies to:

$$I = I_0 \exp \left( -\frac{qV}{nk_BT} \right).$$  \hspace{1cm} (4)

Which can be plotted in an ln($I$)-$V$ scale:

$$\ln (I) = \ln (I_0) + \frac{qV}{nk_BT}. \hspace{1cm} (5)$$

This means that we can find the ideality factor from the slope of the TE regime in the ln($I$)-$V$ plot as the slope equals $q/nk_BT$. Similarly from the intercept of this linear TE regime with the y-axis we can obtain the Schottky barrier height, because the intercept equals $\ln(I_0)$ and:

$$\ln (I_0) = \ln (AA^* T^2) - \frac{q\Phi_B}{k_BT}. \hspace{1cm} (6)$$

The contact area, $A$, is determined from the DMT-model as we have described in previous work.\textsuperscript{12} The tip radius was <20 nm and the force applied was 16.35 nN. This corresponds to a contact area of 9.8 nm$^2$.

From F-N and DT, a product of the Schottky barrier height and the barrier width can be obtained. This product is referred to as the barrier parameter. It should be noted that the barrier parameter of F-N differs from the barrier parameter of DT. In a F-N plot, the
F-N regime can be recognized as it satisfies the linear relation:\textsuperscript{10,13}

\[
\ln \left( \frac{I}{V^2} \right) = \ln \left( \frac{Aq^3m_0}{8\pi h\Phi_Bd^2m^*} \right) - \frac{8\pi\sqrt{2m^*}\Phi_B^{3/2}d}{3hqV}.
\] (7)

The slope of the F-N regime then equals \(-8\pi\sqrt{2m^*}\Phi_B^{3/2}d/3hq\). From this we can extract the barrier parameter of \(\Phi_B^{3/2}d\).

The barrier parameter of DT can also be obtained from the F-N plot. The DT regime satisfies:\textsuperscript{10,13}

\[
\ln \left( \frac{I}{V^2} \right) = \ln \left( \frac{Aq^2\sqrt{2m^*}\Phi_B}{Vh^2d} \right) - \frac{4\pi d\sqrt{2m^*}\Phi_B}{h}.
\] (8)

This means that the data should be fitted with a logarithmic function. The right term in equation 8 then equals \(-4\pi d\sqrt{2m^*}\Phi_B/h\). From which the barrier parameter, \(\sqrt{\Phi_Bd}\), can be obtained.

The fits for all thicknesses (SL, BL, FL, ML) and the two hydration states (1L-H\textsubscript{2}O and 2L-H\textsubscript{2}O) are shown in Figure S7 for three types of fitting; Thermionic emission (\(\ln(I)\) versus \(V\)), Fowler-Nordheim tunneling (\(\ln(I/V^2)\) versus \(1/V\)) and Direct tunneling (\(\ln(I/V^2)\) versus \(\ln(|1/V|)\)). If the injection mechanism is dominated by thermionic emission, this will result in a linear relation in the Thermionic emission plot. Similarly, for Fowler-Nordheim tunneling and direct tunneling, will result in linear relations in the Fowler-Nordheim tunneling and Direct tunneling plots, respectively. The dominating injection mechanisms are the same for SL, BL and FL WS\textsubscript{2}; Fowler-Nordheim tunneling for high positive bias voltages on 2L-H\textsubscript{2}O regions and direct tunneling for negative bias voltages, positive bias voltages on 1L-H\textsubscript{2}O regions and low bias voltages on 2L-H\textsubscript{2}O regions. The measured barrier parameters are presented in Table 1 in the main text. The dominating injection mechanisms for ML WS\textsubscript{2} are different; thermionic emission for low negative bias voltages, Fowler-Nordheim tunneling for high negative bias voltages and high positive bias voltages on 1L-H\textsubscript{2}O and direct tunneling for positive bias voltages on 2L-H\textsubscript{2}O and low positive bias voltages on 1L-H\textsubscript{2}O.
Figure S7: The measured $I(V)$ curves for SL, BL, FL and ML (columns from left to right). The data are plotted in three ways; TE ($\ln(I)$ versus $V$), F-N ($\ln(I/V^2)$ versus $1/V$) and DT ($\ln(I/V^2)$ versus $\ln(1/V)$) (rows from top to bottom). Linear and logarithmic fits are indicated by the black dotted lines.

References

(1) Godin, K.; Cupo, C.; Yang, E.-H. Reduction in Step Height Variation and Correcting Contrast Inversion in Dynamic AFM of WS 2 Monolayers. Scientific Reports 2017, 7, 17798.

(2) Ottaviano, L.; Palleschi, S.; Perrozzi, F.; D’Olimpio, G.; Priante, F.; Donarelli, M.; Benassi, P.; Nardone, M.; Gonchigsuren, M.; Gombosuren, M. et al. Mechanical Exfoliation and Layer Number Identification of MoS2 Revisited. 2D Materials 2017, 4, 045013.
(3) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.

(4) Nemes-Incze, P.; Osváth, Z.; Kamarás, K.; Biró, L. P. Anomalies in Thickness Measurements of Graphene and Few Layer Graphite Crystals by Tapping Mode Atomic Force Microscopy. *Carbon* **2008**, *46*, 1435–1442.

(5) Novoselov, K. S.; Jiang, D.; Schedin, F.; Booth, T. J.; Khotkevich, V. V.; Morozov, S. V.; Geim, A. K.; Rice, T. M. Two-Dimensional Atomic Crystals. *Proceedings of the National Academy of Sciences of the United States of America* **2005**, *102*, 10451–10453.

(6) Britnell, L.; Ribeiro, R. M.; Eckmann, A.; Jalil, R.; Belle, B. D.; Mishchenko, A.; Kim, Y.-J.; Gorbachev, R. V.; Georgiou, T.; Morozov, S. V. et al. Strong Light-Matter Interactions in Heterostructures of Atomically Thin Films. *Science* **2013**, *340*, 1311–1314.

(7) Kuc, A.; Zibouche, N.; Heine, T. Influence of Quantum Confinement on the Electronic Structure of the Transition Metal Sulfide TS₂. *Physical Review B* **2011**, *83*, 245213.

(8) Anwar, A.; Nabet, B.; Culp, J.; Castro, F. Effects of Electron Confinement on Thermionic Emission Current in a Modulation Doped Heterostructure. *Journal of Applied Physics* **1999**, *85*, 2663–2666.

(9) Kim, C.; Moon, I.; Lee, D.; Choi, M. S.; Ahmed, F.; Nam, S.; Cho, Y.; Shin, H.-J.; Park, S.; Yoo, W. J. Fermi Level Pinning at Electrical Metal Contacts of Monolayer Molybdenum Dichalcogenides. *ACS Nano* **2017**, *11*, 1588–1596.

(10) Retamal, J. R. D.; Periyaganounder, D.; Ke, J.-J.; Tsai, M.-L.; He, J.-H. Charge Carrier Injection and Transport Engineering in Two-Dimensional Transition Metal Dichalcogenides. *Chemical Science* **2018**, *9*, 7727–7745.
(11) Rhoderick, E. H. Metal-Semiconductor Contacts. *IEE Proceedings I (Solid-State and Electron Devices)* 1982, 129, 1-14.

(12) Nowakowski, K.; Zandvliet, H. J. W.; Bampoulis, P. Barrier Inhomogeneities in Atomic Contacts on WS2. *Nano Letters* 2019, 19, 1190-1196.

(13) Das, S.; Prakash, A.; Salazar, R.; Appenzeller, J. Toward Low-Power Electronics: Tunneling Phenomena in Transition Metal Dichalcogenides. *ACS Nano* 2014, 8, 1681-1689.