

## Supporting Information

# Visualizing Orbital Content of Electronic Bands in Anisotropic

## 2D Semiconducting ReSe<sub>2</sub>

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## 1. 2D character of valence band structure in ML ReSe<sub>2</sub>

Figure S1 shows photon energy ( $h\nu$ )-dependence of the valence band structure in ML ReSe<sub>2</sub> for both p- and s-polarized light configurations. Energy and momentum positions of the bands do not change for different  $h\nu$  values, although their relative intensities vary due to different cross-sections or geometric effects. The lack of dispersion with  $h\nu$  is consistent with the 2D nature of the electronic structure in the single-layer limit.

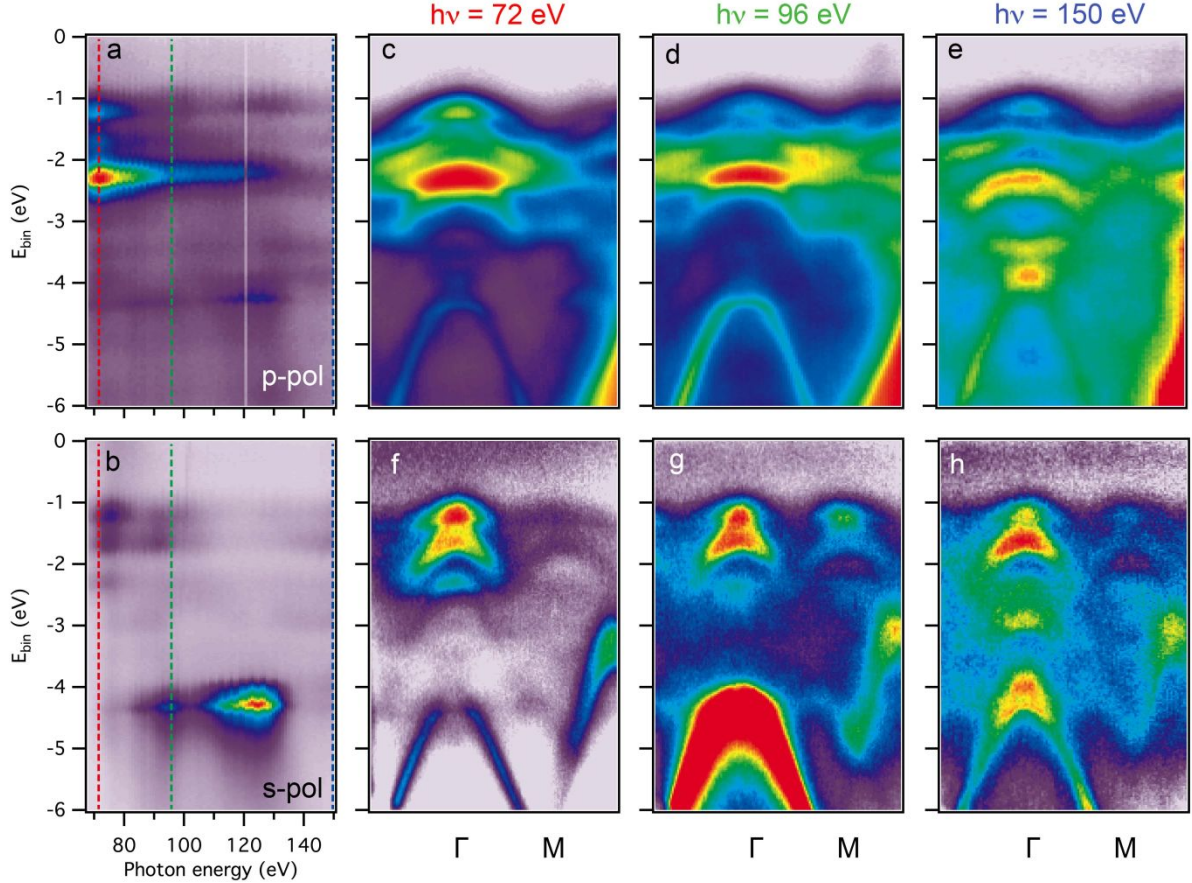


Figure S1. 2D character of valence band structure in ML ReSe<sub>2</sub>. (a,b) Photon energy( $h\nu$ )-dependence of valence band cuts at  $\Gamma$  with p- (a) and s-polarized light (b). (c-e) Valence bands along  $\Gamma$ -M for  $h\nu = 72$  (c), 96 (d), 150 eV (e) using p-polarization. (f-h) Valence bands along  $\Gamma$ -M for  $h\nu = 72$  (f), 96 (g), 150 eV (h) using s-polarization. The 2D electronic structure of the ML ReSe<sub>2</sub> is confirmed by the lack of dispersion with  $h\nu$ .

## 2. Symmetric band structure of ML ReSe<sub>2</sub> along three equivalent axes

Figure S2 shows symmetric valence band structure of ML ReSe<sub>2</sub> along the principal axes ( $\Gamma$ - $M_i$  and  $\Gamma$ - $K_i$  for  $i=1,2,3$ ). The band cuts display similar features along each of the  $\Gamma$ - $M_i$  or  $\Gamma$ - $K_i$  directions, showing their effective equivalence.

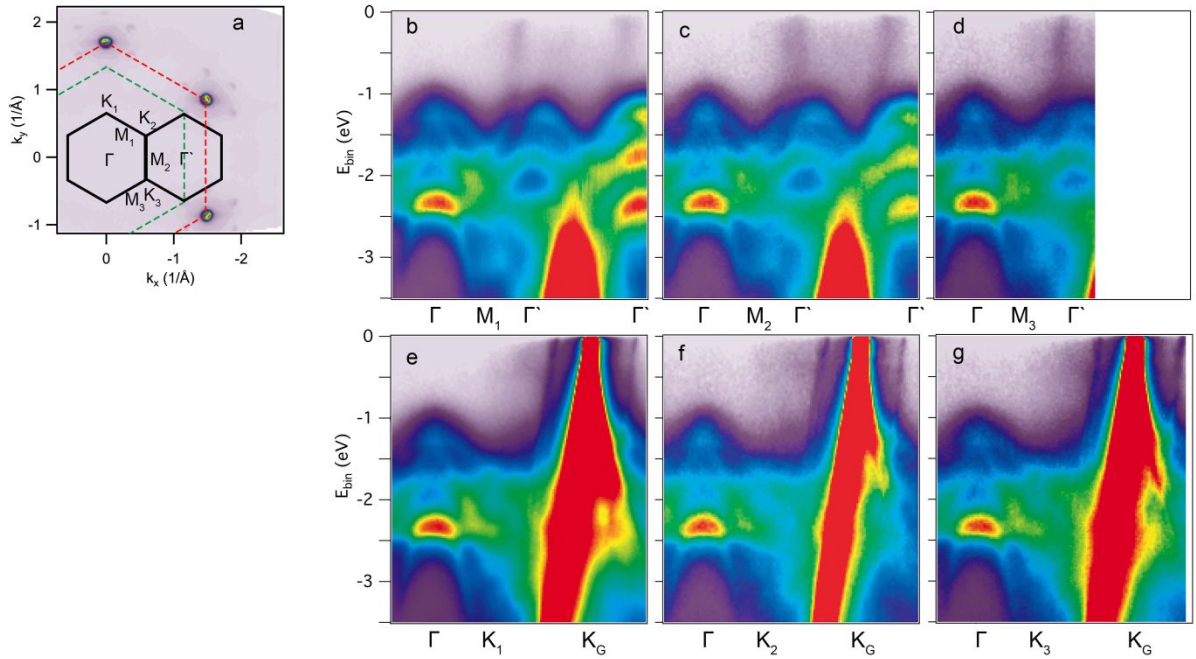


Figure S2. Symmetric valence band structure of ML ReSe<sub>2</sub> along the principal axes. (a) Fermi surface map of ML ReSe<sub>2</sub>. (b-g) Band cuts along  $\Gamma$ - $M_1$  (b),  $\Gamma$ - $M_2$  (c),  $\Gamma$ - $M_3$  (d),  $\Gamma$ - $K_1$  (e),  $\Gamma$ - $K_2$  (f), and  $\Gamma$ - $K_3$  (g) directions. (All spectra here were obtained with the p-polarization and  $h\nu=96$  eV.)

### 3. Valence band maximum analysis during potassium deposition

Figure S3 presents an energy distribution curve (EDC) analysis of a polycrystalline Au spectrum and the ReSe<sub>2</sub> valence band maximum (VBM) during potassium deposition. The EDC extracted from the Au spectrum is fitted by a Fermi-Dirac distribution. VBM fits of ReSe<sub>2</sub> consist of two components (VB1 and VB2) that are described by gaussian functions.

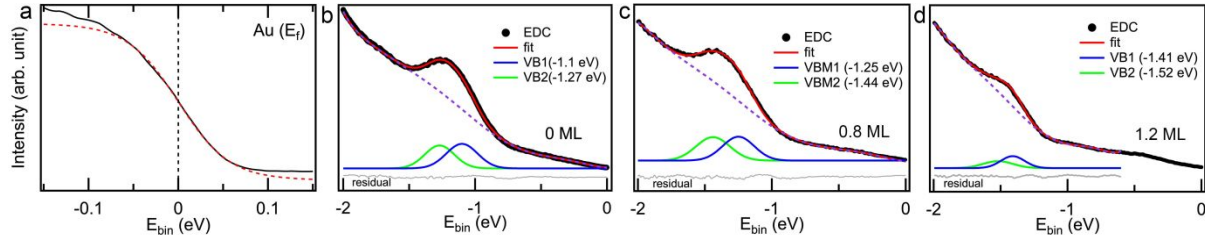


Figure S3. VBM shift during potassium deposition. (a) EDC around the Fermi edge taken on polycrystalline Au in order to calibrate the energy scale. (b-d) VBM fits of ML ReSe<sub>2</sub> spectra for a potassium coverage of 0 ML (b), 0.8 ML (c), and 1.2 ML (d).

#### 4. Temperature dependence of valence band structure in ML ReSe<sub>2</sub> and BLG

Figure S4 presents a comparison between the ARPES spectra taken at sample temperatures of 80 K and 270 K. During the temperature cycle, we observe  $\sim 50$  meV energy shift of the ReSe<sub>2</sub> VBM, which is a relatively small change. This small shift implies that a temperature-induced change of carrier density does not significantly alter the electronic structure of ML ReSe<sub>2</sub> on BLG. We also note that all the measurements were performed at  $\sim 90$  K, so that the temperature effect is minimal for understanding the rest of ARPES results.

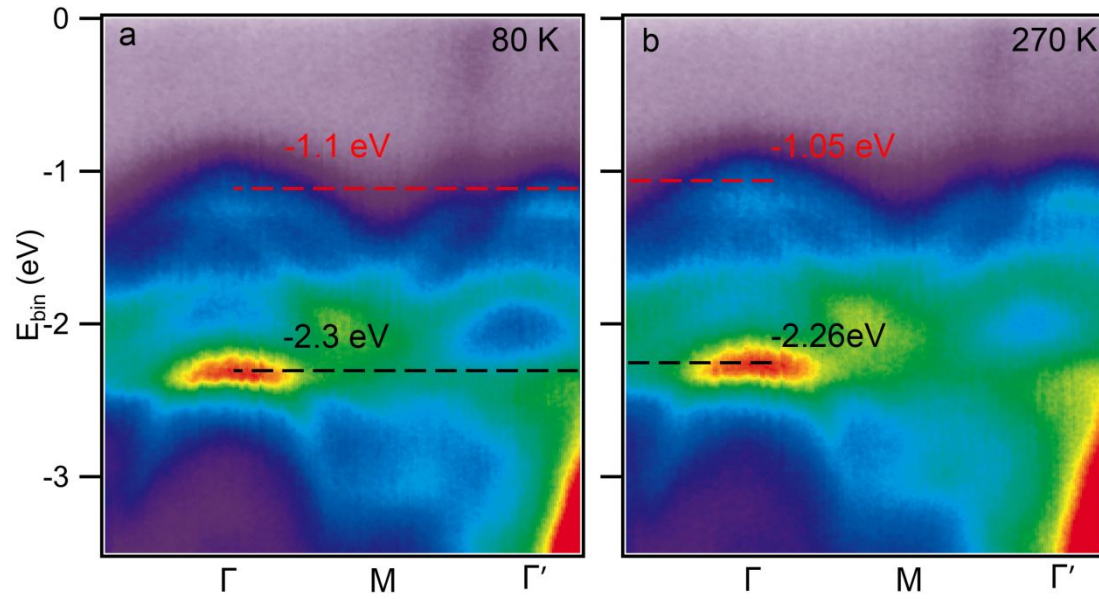


Figure S4. Temperature dependence of valence band structure in ML ReSe<sub>2</sub>. (a,b) ARPES spectra for ML ReSe<sub>2</sub> along  $\Gamma$ -M- $\Gamma'$  at 80 K (a) and 270 K (b).

## 5. Orbital character of valence bands

Figure S5 presents the orbital-projected valence band calculation for a wide momentum range. These orbital projected bands show qualitative agreement with the ARPES spectra in Fig. 3a-d.

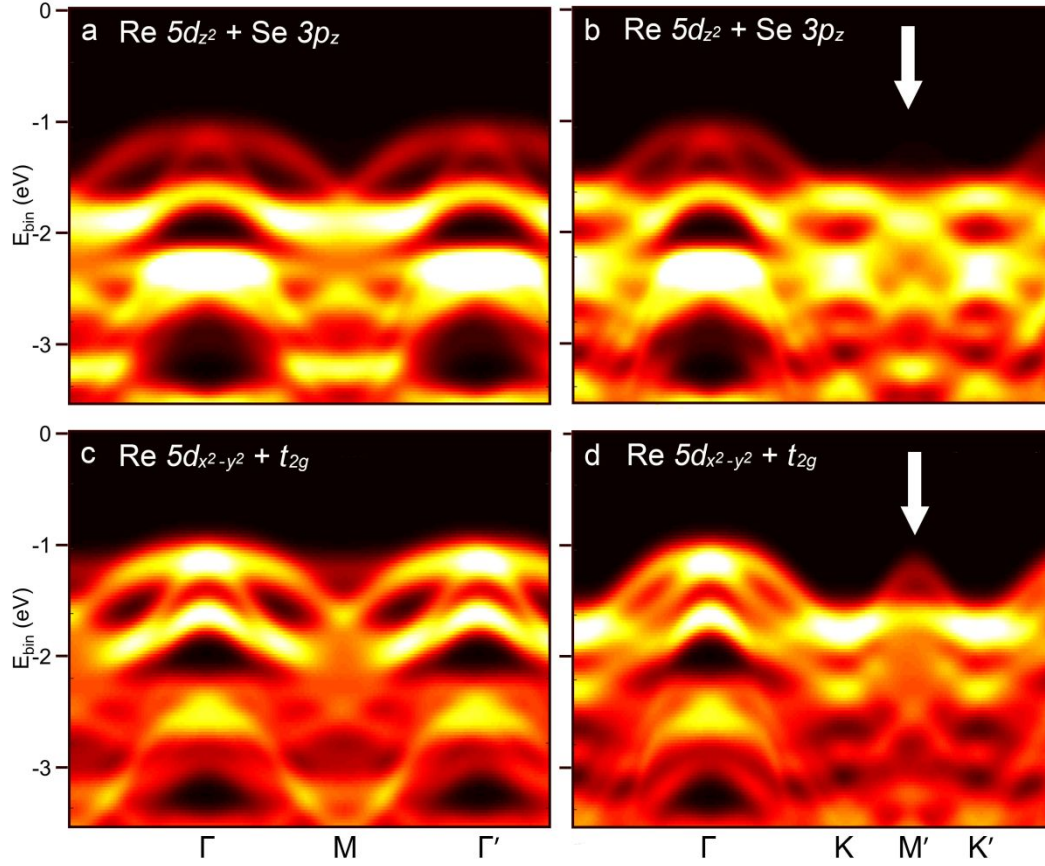


Figure S5. Orbital-projected valence band density of states in ML ReSe<sub>2</sub>. (a,b) Contribution of Re  $5d_{z^2}$  and Se  $3p_z$  orbitals along  $\Gamma$ -M- $\Gamma'$  (a) and  $\Gamma$ -K-M' (b). (c,d) Contribution of Re  $d_{x^2-y^2}$  and  $t_{2g}$  orbitals along  $\Gamma$ -M- $\Gamma'$  (c) and  $\Gamma$ -K-M' (d). The white arrows in (b) and (d) indicate the intensity close to the M' point from electronic states of one of the domains also marked in Fig. 3.

## 6. Surface electron doping *via* potassium deposition

Figure S6 shows X-ray photoemission spectroscopy (XPS) data of potassium ( $3p$ ) and rhenium ( $4f$ ) collected during surface electron doping *via* potassium deposition. The potassium  $3p$  spectra exhibit a systematic intensity increase with potassium coverage. When the second potassium layer forms, an interface peak emerges on the left of the main surface peak. We define potassium density at which the interface peak emerges as one monolayer (1 ML) coverage. During the potassium deposition, the rhenium  $4f$  spectra show an energy shift of  $-0.32$  eV as seen in Fig. S6d, which is consistent with the VBM shift ( $-0.3$  eV) discussed in the main manuscript. It is noted that the small shoulders (Re-Se) on the right side of main peaks are probably caused by the defect phase formed during Se-decapping. These shoulders do not shift during the potassium deposition.

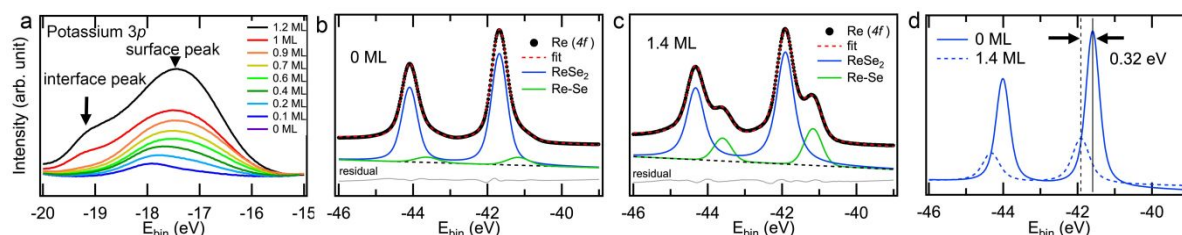


Figure S6. Surface electron doping *via* potassium deposition. (a) XPS data of potassium  $3p$ . (b-d) XPS data of rhenium  $4f$  at a coverage of 0 ML (b) and 1.4 ML (c). (d) Comparison of the main peaks ( $\text{ReSe}_2$ ) for the two coverages.

## 7. Doping dependence of valence band structure in ML ReSe<sub>2</sub> and BLG

Figure S7 presents the valence bands of ReSe<sub>2</sub> and bilayer graphene for different surface potassium doping levels in order to compare the respective band alignments. In the pristine sample, the charge neutrality point of the BLG is given by  $E_N = -0.33$  eV below the Fermi level. In comparison, VBM of ReSe<sub>2</sub> is located at  $E_{VBM} = -1.1$  eV below the Fermi level. At 1.2 ML potassium coverage, the  $E_N$  shifts to  $-0.53$  eV below the Fermi level while the VBM moves to  $E_{VBM} = -1.41$  eV. During the doping, the 2D carrier density of BLG changes from  $1.6 \times 10^{13} \text{ cm}^{-2}$  to  $4.1 \times 10^{13} \text{ cm}^{-2}$  (we estimate these carrier densities by using BLG density of states as provided by a standard tight-binding model), which corresponds to  $2.1 \times 10^{13} \text{ cm}^{-2}$  per ML potassium coverage. Since this carrier density only accounts for the doping of the BLG, the total contributing carrier density from the potassium should also include the doping of ML ReSe<sub>2</sub>.

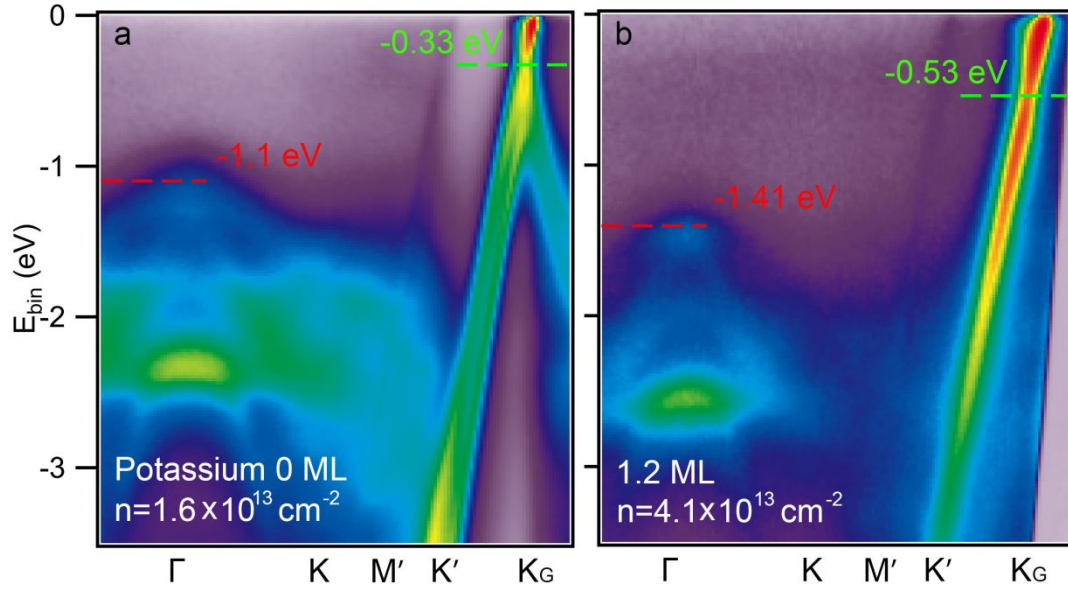


Figure S7. Doping dependence of valence band structure in ML ReSe<sub>2</sub> and BLG. (a,b) ARPES spectra for ML ReSe<sub>2</sub> along  $\Gamma$ -K-M' for potassium coverage of 0 ML (a) and 1.2 ML (b). Red and green dashed lines indicate the VBM of ML ReSe<sub>2</sub> and the neutrality point ( $E_N$ ) of BLG, respectively.