

This item is the archived preprint of:

Prevalence of oxygen defects in an in-plane anisotropic transition metal dichalcogenide

Reference:

Plumadore Ryan, Baskurt Mehmet, Boddison-Chouinard Justin, Lopinski Gregory, Modarresi Mohsen, Potasz Paw el, Haw rylak Paw el, Sahin Hasan, Peeters François, Luican-Mayer Adina.- Prevalence of oxygen defects in an in-plane anisotropic transition metal dichalcogenide Physical review B / American Physical Society - ISSN 2469-9950 - 102:20(2020), 205408 Full text (Publisher's DOI): https://doi.org/10.1103/PHY SREV B.102.205408 To cite this reference: https://hdl.handle.net/10067/1735250151162165141

uantwerpen.be

Institutional repository IRUA

Prevalence of oxygen defects in an in-plane anisotropic transition metal dichalcogenide

Ryan Plumadore¹, Mehmet Baskurt⁵, Justin Boddison-Chouinard¹, Gregory Lopinski², Mohsen Modaresi³, Pawel Potasz⁴, Pawel Hawrylak¹, Hasan Sahin⁵, Francois M. Peeters⁶, Adina Luican-Mayer^{1*}

¹Department of Physics, University of Ottawa, Ottawa, Canada ²National Research Council, Ottawa, Canada ³Department of Physics, Ferdowsi University of Mashhad, Mashhad, Iran ⁴Departmet of Theoretical Physics, Wroclaw University of Science and Technology, Wroclaw, Poland ⁵Deperatment of Photonics, Izmir Institute of Technology, 35430, Urla, Izmir, Turkey ⁶Department of Physics, University of Antwerp, Groenenborgerlaan 171 B-2020 Antwerpen, Belgium

luican-mayer@uottawa.ca

Atomic scale defects in semiconductors enable their technological applications and realization of novel quantum states. Using scanning tunneling microscopy and spectroscopy complemented by ab-initio calculations we determine the nature of defects in the anisotropic van der Waals layered semiconductor ReS₂. We demonstrate the in-plane anisotropy of the lattice by directly visualizing chains of rhenium atoms forming diamond-shaped clusters. Using scanning tunneling spectroscopy we measure the semiconducting gap in the density of states. We reveal the presence of lattice defects and by comparison of their topographic and spectroscopic signatures with ab initio calculations we determine their origin as oxygen atoms absorbed at lattice point defect sites. These results provide an atomic-scale view into the semiconducting transition metal dichalcogenides, paving the way toward understanding and engineering their properties.

Keywords: point defects, scanning tunneling microscopy, TMD, ab-initio

Intrinsic defects, such as grain boundaries, vacancies, adatoms, and substitutional impurities are ubiquitously present in graphene and transition metal dichalcogenides (TMDs)¹⁻⁴. Harnessing the properties of TMDs for atomic scale opto-electronic devices requires detailed understanding of the nature and effects of structural lattice defects on the material properties. Defects can influence the performance of devices through the formation of electronic states within the semiconducting gap ^{5,6}, can modify the excitonic transitions and photoluminescence response⁷, can behave as atom-

like quantum emitters^{8,9} and can affect the catalytic properties¹⁰. Although imaging techniques visualized surface defects of bulk TMDs¹¹⁻¹³, identifying their nature and correlating their presence with properties of the material remains challenging. For example, one of the most common imaging techniques, electron microscopy, can result in knock-on sputtering of chalcogen atoms¹³, making it impossible to distinguish the intrinsic defects. Moreover, in the case of some TMDs like ReS₂, the larger atomic number of the metal can prevent identifying the nature of defects. Therefore, non-invasive techniques like scanning tunneling microscopy and spectroscopy (STM/STS) can be invaluable in imaging and determining the properties of lattice defects.

Here, we use a combination of STM/STS (Figure 1(a)) in tandem with ab initio calculations to determine the structural and electronic properties of ReS_2 and its defects. These experimental and theoretical results indicate that a common defect corresponds to oxygen atoms adsorbed at lattice point defect sites.

While most van der Waals (vdW) layered materials are isotropic within the plane, a number of them have lower in-plane crystal symmetry¹⁴. In-plane anisotropy in layered vdW materials gives additional functionality that has only just began to be explored in black phosphorus $(BP)^{15}$, transition metal trichalcogenides (TiS3)¹⁶, rhenium disulfide (ReS2) and rhenium diselenide (ReSe₂)¹⁷. Among them, ReS₂ attracted attention as a material that is stable under ambient conditions, with structural anisotropy that translates into further tunability in its electronic ^{18,19}, optical ²⁰⁻²³ and mechanical²⁴ properties. Structurally, ReS₂ is a distorted 1T structure which belongs to the $P\overline{1}$ space group ^{25,26}. The additional electron in the d orbital of the rhenium atoms favors the existence of metallic Re-Re bonds, responsible for the formation of a superlattice of chains with diamond clusters of 4 Re atoms, as shown schematically in Figure 1(b). This structure was previously visualized by X-ray spectroscopy^{25,27} and electron microscopy¹³. Early scanning probe microscopies provided also indications of a Re chain structure ²⁸⁻³⁰. When cleaved, the crystal orientation of the ReS₂ flakes is apparent, as they maintain the edges parallel to the rhenium chains. This feature is useful for identifying the orientation of a crystal for example in device fabrication ^{18,31}. Indeed, in the large area STM topographic images, as presented in Figure 1(c), we find that terraces on the surface of ReS₂ follow the crystallographic directions with an angle $\gamma \approx$ 120° between the a and b directions. The terraces and steps in Figure 1(c) correspond to single or double atomic layers, with their height measured as shown in the inset.

In higher resolution images, presented in Figure 1(d), we observe the characteristic anisotropic lattice structure with elongated chains. One might be tempted to attribute the measured features to the topmost layer of sulfur (S) atoms³⁰ which is closest to the tip. However, a more accurate interpretation reveals that the contrast in the atomically resolved STM topographic images originates from local density of states (LDOS). Therefore, the complex dependence of the partial density of states (PDOS) at the surface layer on the energy at which the tunneling process occurs must be considered. The calculated PDOS using ab initio theory is shown in Figure 1(e). The density of states is dominated by the Rhenium-d orbitals, which is related to the flat band



Figure 1: (a) Schematic of the STM experiment (b) Top and side view of the ReS₂ structure. (c) STM topographic map of step edges on the surface of a ReS₂ crystal (V_b = -1.60V; I_T = 450pA). Inset: Height profile along the white dotted line. (d) STM topographic image highlighting the Re chains with a spheres model as a guide to the eye. (e) Calculated PDOS of monolayer ReS₂. (f) Simulated STM image of the ReS₂ lattice.

dispersion around the top of the valence band (VB) at the Γ point. At higher energies, band crossings lead to a substructure in the density of states. We find that within the energy range of our experiment the Rhenium d-orbitals (in red in Figure 1(e)) are responsible for the largest contribution to the density of states. This implies that the metal atoms are predominantly involved in the tunneling process and therefore provide the contrast in the atomically resolved topographic images. This is further confirmed by simulated images of the STM measurement in Figure 1(f).



Figure 2: (a) Scanning Tunneling Spectroscopy averaged on the surface of ReS₂. The logarithmic scale was used to highlight valence band (VB) and, conduction band (CB) whose band edges relative to the Fermi level (E_F) are also indicated by arrows. (b) Right - line map of the scanning tunneling spectrum across the dashed line indicated in the topographic image in the left (V_b = -1.00V; I_T = 65pA). (c) Band structure of 3-layer ReS₂ and the corresponding DOS.

We now turn our attention to the band structure of ReS₂. Electronically, ReS₂ is a semiconductor, however, the nature of the semiconducting gap (direct or indirect) in the bulk versus monolayers remains a subject of discussion both experimentally and theoretically^{13,32-39}. A number of experimental techniques including optical spectroscopies and electronic transport found the bulk band gap to be in the range of 1.40 ± 0.07 eV ^{13,15,17,18,40} in agreement with results of theoretical

calculations which reported the band gap to be in the range of 1.4 ± 0.1 eV $^{14,16,19,20,13,34-39}$. However, transport and optical spectroscopy are macroscopic measurements which average over large areas of a crystal. Here, we use a local probe, scanning tunneling microscopy and spectroscopy to measure the density of states on the surface of ReS₂ crystals. We find that the differential conductance, in Figure 2(a), shows the presence of an energy gap confirming the semiconducting nature of ReS₂. The extracted value of the energy gap is $1.35 \pm 0.1 \text{ eV}$, agreeing with previous experiments. We note that this spectrum, Figure 2(a), represents averages over different samples, areas, and tips as detailed in Supplemental Figure 1 and it is plotted on a logarithmic scale⁴¹, for clarity. In Figure 2(b) we show the spatial variation of the spectrum across device-size area, topographically presented in the left panel by plotting the scanning tunneling spectra across the dashed line (right panel). Within our resolution, the variation of the energy gap is less than 0.1 eV. These experimental findings are now compared with our theoretical calculations. In Figure 2(c) we show the band structure and corresponding DOS of a slab of ReS₂ consisting of three layers with details of calculations in the supplemental material. The calculations show a gap at the Γ point, and from the corresponding DOS we can estimate the energy gap around $E_{gap}=1.3$ eV, in good agreement with the measured semiconducting energy gap. While the DFT gap appears to be in good agreement with the measured semiconducting energy gap, we note that DFT underestimates the energy gap. Inclusion of many-body corrections at the G0W0 quasiparticle level increases the bandgap to 2.3eV. However, we note that the blue shift of quasiparticle transition energies is partially compensated by excitonic effects which reduces the optical gaps to values often consistent with DFT bandgaps. In a STS measurement, the zero bias corresponds to the Fermi level (E_F) as indicated by the dashed line in Figure 2(a). In an electrically neutral ReS_2 , we expect the position of E_F to be in the middle of the semiconducting gap. However, in our samples we find the position of E_F to be close to the bottom of the conduction band (E_C), indicating the crystal is n-doped.

We now turn to the analysis of dopants and defects. When imaging the surface of the ReS₂ crystal, we encounter "bright" or "dark" regions representing the presence of a dopant or defect that will electrostatically interact with its environment. Such features have been previously reported on surfaces of doped III-V semiconductors⁴², topological insulators⁴³, transition metal dichalcogenides⁴⁴, BP^{45,46} or BN⁴⁷. The most common type of defects are shown in the STM topographic image of Figure 3(a). They have a characteristic bright center with a dark halo when imaged at negative bias voltages (Figure 3(b)). As we vary the scanning parameters, we observe that the apparent height of the defects changes, so that they appear bright at negative bias voltages and dark at positive bias voltages. This is demonstrated in Figure 3(c) where we present STM topographic images taken at different bias voltages: -0.80 V, and +0.80 V respectively. The



Figure 3: (a) STM topographic image (V_b = -1.20V; I_T = 80pA) showing lattice defects. (b) Topographic high resolution image across a defect. Inset: LDOS map across a defect at V_B = -1.2V and I_T = 35pA. (c) STM topographic images (I_T = 50pA) of an area at different bias voltages. Top: V_{bias} = -0.80V; bottom: V_{bias} = +0.80 V. (d) Measured STS on the defect in (b).

spectroscopic data acquired on the center of the defect, presented in Figure 3(d), closely resembles the one on a defect-free area, and reveals the absence of in-gap states. The slight increase in DOS within the gap could be due to buried defects under the surface⁴⁸. To complement our STM/STS data, we performed XPS analysis of the crystal and, in addition to the expected Re and S we also find the presence of oxygen (Supplemental Figure 4).

Different possible atomic scale defects in the lattice of ReS_2 can have signatures in an STM experiment. For example, defects such as a single atom vacancy, single atom adsorption, antisite formation where S atom is substituted by Re atom or vice-versa can be formed during the growth of 2D ReS₂ sheets. To elucidate the possible origins of the most common defects observed in our STM experiments on the surface of ReS₂ we used DFT calculations. Simulated STM images of pristine ReS₂ and defected structures, together with their characteristic density of states, are presented in Figure 4.



Figure 4: Crystal structure and simulated STM images of (a) S-vacancy and (b) O absorbed by S-vacancy. (c) LDOS of S-vacancy and O absorbed by S-vacancy.

The results of ab-initio calculation indictate that Sulfur vacancy, as shown in Figure 4(a), would result in a dark feature in the LDOS, different from the observed common defect. The lack of features characteristic of S vacancy would seem surprising given that previous calculations suggested that sulfur S vacancies have the lowest formation energy⁴⁹. However, we propose that

the formation of such defects results in dangling bonds within the lattice, which are readily oxygenated under atmospheric conditions, leading to O atom absorption by vacancies within the lattice. In fact, our theoretical results show that Oxygen absorption by an S-vacancy, as presented in Figure 4(b), will create signatures in the density of states maps that closely resemble the measured defects, with a distinctive halo structure. Moreover, when we examine the density of states, a S-vacancy results in mid-gap states (red curve in Figure 4(c)), while when an O atom is bound to the S vacancy, the semiconducting band gap changes only slightly, in agreement with our experimental finding from STS presented in Figure 3(e), strengthening the case for oxygen being a common defect in the ReS₂ layers. These results are also consistent with the reports that oxygen is a source of atomic-scale defects in $MoS_2^{11,12}$.

We note that in addition to the defects discussed in Figure 3, we also observed less frequent types of lattice defects as discussed in the supplemental material.

In summary, we presented results of scanning tunneling microscopy and spectroscopy together with ab initio DFT calculations of the nanoscale lattice structure, electronic bandgap and defects of in-plane anisotropic semiconducting ReS₂. We resolve the chains of rhenium atoms forming diamond-shaped clusters, we measure the semiconducting energy gap and compare the experimental values with results of ab initio calculations. Moreover, we reveal the presence of atomic lattice defects and explore their local properties. By comparing their signatures in the STM/STS experiment with the theoretical calculations, we identify that oxygen is frequently absorbed at defect sites in this material. As the nature of atomic defects is critical in understanding the properties of 2D materials, our result paves the way toward understanding and engineering properties of in-plane anisotropic 2D semiconductors.

Methods:

Theory - The calculations of energy bands, the bandgap and density of states in a single layer and a slab consisting of 3 layers of ReS₂ were done using the Quantum Espresso code, with cut-off energy 70 Ry and mesh of 25*25*1 k-grid. Each layer/slab was separated by 20 Å of vacuum and the structure was fully relaxed. Vienna *ab-initio* Simulation Package (VASP) and plane-wave projector-augmented wave (PAW) potentials were used in the calculations.⁴⁷ Generalized gradient approximation (GGA) form of Perdew-Burke-Ernzerhof (PBE) was used for the exchange-

correlation functional.⁴⁸ Kinetic energy cut-off of the plane-wave basis set was taken to be 400 eV. For the structural optimization and LDOS calculations a Gaussian broadening width of 0.05 eV was taken. The convergence criterion between consequent electronic steps was set at 10^{-5} eV. Gamma centered k-mesh was taken as 5x5x1 and 10x10x1 for structural optimization and LDOS calculations, respectively, for 2x2x1 supercell. At least 15 Å of vacuum spacing between layers was taken in order to prevent any interactions between layers. STM images were simulated by calculating partial charge densities in the range [-2, 0] and [-2, 2] eV of the cells, and using the formula:

$$E_{total} = \sum_{n}^{h} E_{n} e^{-kz_{n}}$$

where E_{total} is the summed charge density matrix, n is the layer number, h is the height of the ReS₂ monolayer, E_n is the nth layer partial charge density matrix, k is a constant, and z_n is the distance from the artificial STM tip in the z direction. Contrast changes as a results of the bias voltage were simulated by involving electron doped conduction bands in a range of 2 eV.

STM/STS We use a commercial RHK Pan Freedom system with ultrahigh vacuum (UHV) and variable temperature capabilities. The data here are taken at temperatures 80K-300K.

Sample preparation In this study we use commercial (HQ Graphene) bulk crystals ReS₂ cleaved in air and subsequently introduced into ultrahigh vacuum (UHV).

XPS The XPS spectra were measured on a Kratos Axis Nova spectrometer equipped with an Al X-ray source. The XPS data were collected using AlKα radiation at 1486.69 eV (150 W, 10 mA), charge neutralizer and a delay-line detector (DLD) consisting of three multi-channel plates.

Acknowledgement

The authors acknowledge funding from the National Sciences and Engineering Research Council (NSERC) Discovery Grant RGPIN-2016-06717. We also acknowledge the support of the Natural Sciences and Engineering Research Council of Canada (NSERC) through QC2DM Strategic Project STPGP 521420. PH thanks uOttawa Research Chair in Quantum Theory of Materials for support. PP acknowledges partial financial support from National Science Center (NCN), Poland,

grant Maestro No. 2014/14/A/ST3/00654 and calculations were performed in the Wrocław Center for Networking and Supercomputing.

H.S. Acknowledges financial support from TUBITAK under the project number 117F095 and from Turkish Academy of Sciences under the GEBIP program. Our computational resources were provided by TUBITAK ULAKBIM, High Performance and Grid Computing Center (TR-Grid e-Infrastructure).

References

- 1 Manzeli, S., Ovchinnikov, D., Pasquier, D., Yazyev, O. V. & Kis, A. 2D transition metal dichalcogenides. *Nature Reviews Materials* **2**, 17033, doi:10.1038/natrevmats.2017.33 (2017).
- Lin, Z. *et al.* Defect engineering of two-dimensional transition metal dichalcogenides. *2D Materials* 3, 022002 (2016).
- Luican-Mayer, A. *et al.* Localized electronic states at grain boundaries on the surface of graphene and graphite. *2D Materials* **3**, 031005, doi:10.1088/2053-1583/3/3/031005 (2016).
- 4 Luican-Mayer, A., Li, G. & Andrei, E. Y. Atomic scale characterization of mismatched graphene layers. *Journal of Electron Spectroscopy and Related Phenomena* **219**, 92-98, doi:<u>https://doi.org/10.1016/j.elspec.2017.01.005</u> (2017).
- 5 Qiu, H. *et al.* Hopping transport through defect-induced localized states in molybdenum disulphide. *Nature Communications* **4**, 2642, doi:10.1038/ncomms3642 (2013).
- 6 Shim, J. *et al.* Phosphorene/rhenium disulfide heterojunction-based negative differential resistance device for multi-valued logic. *Nature Communications* **7**, 13413, doi:10.1038/ncomms13413 (2016).
- 7 Tongay, S. *et al.* Defects activated photoluminescence in two-dimensional semiconductors: interplay between bound, charged and free excitons. *Scientific Reports* **3**, 2657, doi:10.1038/srep02657 (2013).
- 8 Atatüre, M., Englund, D., Vamivakas, N., Lee, S.-Y. & Wrachtrup, J. Material platforms for spinbased photonic quantum technologies. *Nature Reviews Materials* **3**, 38-51, doi:10.1038/s41578-018-0008-9 (2018).
- 9 Grosso, G. *et al.* Tunable and high-purity room temperature single-photon emission from atomic defects in hexagonal boron nitride. *Nature Communications* **8**, 705, doi:10.1038/s41467-017-00810-2 (2017).
- 10 Zhou, Y. *et al.* Auto-optimizing Hydrogen Evolution Catalytic Activity of ReS2 through Intrinsic Charge Engineering. *ACS Nano* **12**, 4486-4493, doi:10.1021/acsnano.8b00693 (2018).

- 11 Barja, S. *et al.* Identifying substitutional oxygen as a prolific point defect in monolayer transition metal dichalcogenides. *Nature Communications* **10**, 3382, doi:10.1038/s41467-019-11342-2 (2019).
- 12 Schuler, B. *et al.* Large Spin-Orbit Splitting of Deep In-Gap Defect States of Engineered Sulfur Vacancies in Monolayer WS₂ *Physical Review Letters* **123**, 076801, doi:10.1103/PhysRevLett.123.076801 (2019).
- 13 Lin, Y.-C. *et al.* Single-Layer ReS2: Two-Dimensional Semiconductor with Tunable In-Plane Anisotropy. *ACS Nano* **9**, 11249-11257, doi:10.1021/acsnano.5b04851 (2015).
- 14 Wilson, J. A. & Yoffe, A. D. The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties. *Advances in Physics* **18**, 193-335, doi:10.1080/00018736900101307 (1969).
- Ling, X., Wang, H., Huang, S., Xia, F. & Dresselhaus, M. S. The renaissance of black phosphorus. *Proceedings of the National Academy of Sciences* **112**, 4523-4530, doi:10.1073/pnas.1416581112 (2015).
- 16 Dai, J. & Zeng, X. C. Titanium Trisulfide Monolayer: Theoretical Prediction of a New Direct-Gap Semiconductor with High and Anisotropic Carrier Mobility. *Angewandte Chemie International Edition* **54**, 7572-7576, doi:10.1002/anie.201502107 (2015).
- 17 Rahman, M., Davey, K. & Qiao, S.-Z. Advent of 2D Rhenium Disulfide (ReS2): Fundamentals to Applications. *Advanced Functional Materials* **27**, 1606129-n/a, doi:10.1002/adfm.201606129 (2017).
- 18 Liu, E. *et al.* Integrated digital inverters based on two-dimensional anisotropic ReS2 field-effect transistors. *Nature Communications* **6**, 6991, doi:10.1038/ncomms7991

https://www.nature.com/articles/ncomms7991#supplementary-information (2015).

19 Ovchinnikov, D. *et al.* Disorder engineering and conductivity dome in ReS2 with electrolyte gating. *Nature Communications* **7**, 12391, doi:10.1038/ncomms12391

https://www.nature.com/articles/ncomms12391#supplementary-information (2016).

- 20 Chenet, D. A. *et al.* In-Plane Anisotropy in Mono- and Few-Layer ReS₂ Probed by Raman Spectroscopy and Scanning Transmission Electron Microscopy. *Nano Letters* **15**, 5667-5672, doi:10.1021/acs.nanolett.5b00910 (2015).
- 21 Aslan, O. B., Chenet, D. A., van der Zande, A. M., Hone, J. C. & Heinz, T. F. Linearly Polarized Excitons in Single- and Few-Layer ReS2 Crystals. *ACS Photonics* **3**, 96-101, doi:10.1021/acsphotonics.5b00486 (2016).
- 22 Ho, C. H., Huang, Y. S., Tiong, K. K. & Liao, P. C. Absorption-edge anisotropy in ReS₂ and ReSe₂ layered semiconductors. *Physical Review B* **58**, 16130-16135, doi:10.1103/PhysRevB.58.16130 (1998).
- 23 Sim, S. *et al.* Ultrafast quantum beats of anisotropic excitons in atomically thin ReS2. *Nature Communications* **9**, 351, doi:10.1038/s41467-017-02802-8 (2018).
- 24 Yu, S. *et al.* Strain-engineering the anisotropic electrical conductance in ReS2 monolayer. *Applied Physics Letters* **108**, 191901, doi:10.1063/1.4947195 (2016).
- Lamfers, H. J., Meetsma, A., Wiegers, G. A. & de Boer, J. L. The crystal structure of some rhenium and technetium dichalcogenides. *Journal of Alloys and Compounds* **241**, 34-39, doi:<u>https://doi.org/10.1016/0925-8388(96)02313-4</u> (1996).
- 26 Murray, H. H., Kelty, S. P., Chianelli, R. R. & Day, C. S. Structure of Rhenium Disulfide. *Inorganic Chemistry* **33**, 4418-4420, doi:10.1021/ic00097a037 (1994).
- 27 Jariwala, B. *et al.* Synthesis and Characterization of ReS2 and ReSe2 Layered Chalcogenide Single Crystals. *Chemistry of Materials* **28**, 3352-3359, doi:10.1021/acs.chemmater.6b00364 (2016).

- 28 Kelty, S. P., Ruppert, A. F., Chianelli, R. R., Ren, J. & Whangbo, M. H. Scanning Probe Microscopy Study of Layered Dichalcogenide ReS2. *Journal of the American Chemical Society* **116**, 7857-7863, doi:10.1021/ja00096a048 (1994).
- 29 Friemelt, K. *et al.* Scanning tunneling microscopy with atomic resolution on ReS2 single crystals grown by vapor phase transport. *Annalen der Physik* **504**, 248-253, doi:10.1002/andp.19925040403 (1992).
- 30 Jung, S. J. *et al.* Atomic-registry-dependent electronic structures of sulfur vacancies in ReS2 studied by scanning tunneling microscopy/spectroscopy. *Current Applied Physics* **19**, 224-229, doi:<u>https://doi.org/10.1016/j.cap.2018.07.017</u> (2019).
- Liu, F. *et al.* Highly Sensitive Detection of Polarized Light Using Anisotropic 2D ReS2. *Advanced Functional Materials* **26**, 1169-1177, doi:10.1002/adfm.201504546 (2016).
- 32 Webb, J. L. *et al.* Electronic band structure of ReS2 by high-resolution angle-resolved photoemission spectroscopy. *Physical Review B* **96**, 115205, doi:10.1103/PhysRevB.96.115205 (2017).
- 33 Zhong, H.-X., Gao, S., Shi, J.-J. & Yang, L. Quasiparticle band gaps, excitonic effects, and anisotropic optical properties of the monolayer distorted \$1T\$ diamond-chain structures ReS2 and ReSe2. *Physical Review B* **92**, 115438, doi:10.1103/PhysRevB.92.115438 (2015).
- 34 Ignacio, G.-L., Bojja Aditya, R., Nicolas, U. & Alberto, F. M. Electroluminescence from indirect band gap semiconductor ReS 2. *2D Materials* **3**, 045016 (2016).
- 35 Gehlmann, M. *et al.* Direct Observation of the Band Gap Transition in Atomically Thin ReS2. *Nano Letters* **17**, 5187-5192, doi:10.1021/acs.nanolett.7b00627 (2017).
- ³⁶Dileep, K., Sahu, R., Sarkar, S., Peter, S. C. & Datta, R. Layer specific optical band gap measurement at nanoscale in MoS2 and ReS2 van der Waals compounds by high resolution electron energy loss spectroscopy. *Journal of Applied Physics* **119**, 114309, doi:10.1063/1.4944431 (2016).
- 37 Ho, C. H., Liao, P. C., Huang, Y. S., Yang, T. R. & Tiong, K. K. Optical absorption of ReS2 and ReSe2 single crystals. *Journal of Applied Physics* **81**, 6380-6383, doi:10.1063/1.365357 (1997).
- 38 Cakr, D., Sahin, H. & Peeters, F. M. Doping of rhenium disulfide monolayers: a systematic first principles study. *Physical Chemistry Chemical Physics* **16**, 16771-16779, doi:10.1039/C4CP02007C (2014).
- 39 Yu, Z. G., Cai, Y. & Zhang, Y.-W. Robust Direct Bandgap Characteristics of One- and Two-Dimensional ReS2. *Scientific Reports* **5**, 13783, doi:10.1038/srep13783

https://www.nature.com/articles/srep13783#supplementary-information (2015).

- 40 Marzik, J. V., Kershaw, R., Dwight, K. & Wold, A. Photoelectronic properties of ReS2 and ReS22 single crystals. *Journal of Solid State Chemistry* **51**, 170-175, doi:<u>https://doi.org/10.1016/0022-4596(84)90330-X</u> (1984).
- 41 Ugeda, M. M. *et al.* Giant bandgap renormalization and excitonic effects in a monolayer transition metal dichalcogenide semiconductor. *Nature Materials* **13**, 1091-1095, doi:10.1038/nmat4061 (2014).
- 42 Feenstra, R. M. Tunneling spectroscopy of the (110) surface of direct-gap III-V semiconductors. *Physical Review B* **50**, 4561-4570 (1994).
- 43 Hor, Y. S. *et al.* p-type Bi2Se3 for topological insulator and low-temperature thermoelectric applications. *Physical Review B* **79**, 195208, doi:10.1103/PhysRevB.79.195208 (2009).
- 44 Lu, C.-P., Li, G., Mao, J., Wang, L.-M. & Andrei, E. Y. Bandgap, Mid-Gap States, and Gating Effects in MoS2. *Nano Letters* **14**, 4628-4633, doi:10.1021/nl501659n (2014).
- 45 Kiraly, B., Hauptmann, N., Rudenko, A. N., Katsnelson, M. I. & Khajetoorians, A. A. Probing Single Vacancies in Black Phosphorus at the Atomic Level. *Nano Letters* **17**, 3607-3612, doi:10.1021/acs.nanolett.7b00766 (2017).

- 46 Qiu, Z. *et al.* Resolving the Spatial Structures of Bound Hole States in Black Phosphorus. *Nano Letters* **17**, 6935-6940, doi:10.1021/acs.nanolett.7b03356 (2017).
- 47 Wong, D. *et al.* Characterization and manipulation of individual defects in insulating hexagonal boron nitride using scanning tunnelling microscopy. *Nature Nanotechnology* **10**, 949, doi:10.1038/nnano.2015.188

https://www.nature.com/articles/nnano.2015.188#supplementary-information (2015).

- 48 Addou, R., Colombo, L. & Wallace, R. M. Surface Defects on Natural MoS2. *ACS Applied Materials* & Interfaces **7**, 11921-11929, doi:10.1021/acsami.5b01778 (2015).
- 49 Horzum, S. *et al.* Formation and stability of point defects in monolayer rhenium disulfide. *Physical Review B* **89**, 155433, doi:10.1103/PhysRevB.89.155433 (2014).

Supplementary Information for

Prevalence of oxygen defects in an in-plane anisotropic transition metal dichalcogenide Plumadore et al.

1. Scanning Tunneling spectroscopy

Details about the measured variation in the measured band gap across different samples and areas using several tips.



Supplementary Figure 1: Measured bandgap of the ReS₂ for different crystals, areas on a crystal and tips. Error bars reflect uncertainty in identifying the band edges in the STS spectra.

2. Other defects observed in the STM topographic images and LDOS maps

In addition to the common defect described in detail in Figure 3 of the main text (Type A) we also encountered other types of defects indicated in Supplementary Figure 2(a) as Type B and Type C. At negative bias voltages Type B appears bright and Type C appears dark. The relative amount of such defects over an area of $4.7\mu m^2$ is presented in Supplementary Figure 2(b) as a histogram, demonstrating that Type A defects are the most commonly present. Supplementary Figure 2(c) shows the change in contrast for Type A defects when the bias voltage changes sign. The characteristics of the dI/dV maps are also different as shown in Supplementary Figure 2(d).



Supplementary Figure 2: (a) STM topographic image (V_b = -1.20V; I_T = 50pA) with different types of defects labeled A, B, C. (b) Histogram of number of defects of each type encountered by scanning a total area of 4.7 μ m². (c) STM topographic images (I_T = 50pA) of another area taken at indicated bias voltages. (d) STM topographic image (left) (V_b = -0.86 V; I_T =35.0 pA) and its corresponding dI/dV map at -0.86V (right).

3. Details of the theoretical calculation of the signatures of defects

Guided by the signature in the STM images, we explored theoretically the origins of the defects type B and C. In Supplementary Figure 3 we present the results obtained for simulated STM images, calculated LDOS for the indicated type of defects, also illustrated by their lattice structure



Supplementary Figure 3: Simulated STM images and LDOS with crystal structure as inset for (a) O adsorbed on pristine ReS₂, (b) S-vacancy, (c) Re-antisite, (d) Re-vacancy, (e) O adsorbed on S-antisite (f) S-antisite.

in the insets. The type of defects that can show bright contrast in the simulated STM images are oxygen adsorbed on pristine ReS_2 and Re- antisite presented in Supplementary Figure 3(a) and Supplementary Figure 2(b) respectively. For Type C defects that appear darker in topographic images, the possible origins were identified as S-vacancy, Re-vacancy and S-antisite as shown by Supplementary Figure 3(c)-(e). We note that a similar topographic feature of a bright center with dark halo as type A defect was calculated to correspond to oxygen absorbed on a S-antisite. However, based on the comparison with the spectroscopic feature of Figure 3(e), we can conclude that this is not the origin of type A defect.

4. Effect of number of layers and stacking on the calculated energy gap

To verify the effect of the number of layers on the energy gap we carry out ab-initio calculations of a slab consisting of 3 layers. In order to obtain the lowest energy stacking configuration, we consider different starting configurations AAA, ABA, ABB and ABC. To ensure that we obtain the lowest energy configuration we follow two relaxation protocols. In the first method, we relax the monolayer ReS₂ and let a lattice cell orient in a desired direction in space. One of the consequences is that the "Z lattice parameter" has a small deviation from the "Z axis". We then put another layer above the first layer in AA or AB configuration and relax the cell again. In the third step, we put the third layer in ABA, ABB or AAA sequence and relax the structures. At the end, we find the structure with the lowest energy. We observe that initial ABA stacking changes into ABC stacking after relaxation which turns out to have the lowest energy.

In the second method, we first relax the monolayer and freeze "Z lattice parameter" direction along Z axis. We make AA and AB stacking, and create bulk crystal and relaxed it. The lattice constant of bulk in Z direction increases to avoid interaction with the next nearest unit-cells. From such relaxed bulk, we take AB stacking bilayer and add another layer above, making ABA stacking of 3 layers. After relaxation we obtain the total energy which is nearly 15 meV/chemical-unit lower as compared with the energy obtained from the first method. However, the energy difference between the two different stackings of 3 layers (ABA and ABC) is small and we do not exclude a mixture of them at room temperature. In Fig. 2(c) we show the band structure for ABA stacked 3 layer ReS₂ for wave-vector k from M to Γ to K. We see that the valence band maximum is at the Γ point with direct Kohn-Sham energy bandgap between CB and VB of 1.3 eV. However, stacking of layers as we move away from the surface inside the bulk and how the stacking affects the bandgap is not clear. The bulk and single layer bandgaps were found to be very similar which was one of the arguments for the layer independent properties of ReS₂. We note however that the peak in the density of states at the edge of the valence band disappears for the 3 layer system which may explain the absence of the experimental observation of this sharp peak. However, the absence of the peak may be related to the presence of impurities. Additional studies are needed to improve agreement between experiment and theory but the measured and calculated bandgap of ReS₂ ~1.4eV agree very well.

5. Further details of the XPS characterization

The XPS spectra were measured on a Kratos Axis Nova spectrometer equipped with an Al X-ray source. The XPS data were collected using AlKα radiation at 1486.69 eV (150 W, 10 mA), charge neutralizer and a delay-line detector (DLD) consisting of three multi-channel plates.

Upon analysis, we find the Re 4f core level spectra positions at 42.6eV (4f 7/2) and 45 eV (4f 5/2), consistent with literature for exfoliated ReS₂ ^{1,2}. The S 2p core level region can be fit by two S 2p 3/2 and 1/2 doublets (163.3eV, 164.5eV) and (162.6, 163.8eV) as reported previously and attributed to the 1T-ReS₂ structure^{1,2}. In addition, we also find the presence of oxygen, consistent with our interpretation of the measured atomic defects (Supplementary Figure 4).



Supplementary Figure 4: High resolution XPS spectra of Re4f, S2p and O1s regions

Supplementary references

- 1. Khosravi et al., Materials 2019, 12, 1056
- 2. Fujita et al., Nanoscale 2014, 6, 12458