Supplementary Information

Electronic Structure of Thin MoS₂ Films

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Figure S1: Stitched SEM images showing the SI substrate covered with MoS₂. The individual SEM images are numbered consecutively. There is medium coverage with

 MoS_2 for images 9 – 11, 14 – 18, 25 – 30, 37 – 36 and 42. There is high coverage with MoS_2 for images 23 – 24, 31 – 32 and 38 – 41. The overall size of the sample is approximately 10 x 10 mm².





Figure S2: a) SEM image of MoS_2 with labels of interest for Auger spectroscopy, b) Auger spectra for positions 1 (bottom) to 5 (top). In particular spectrum 5 is taken at a location where a triangular shaped crystal can be identified providing evidence that the deposited material is MoS_2 .



Figure S3: VB cut-off region of MoS₂ as measured with UPS.

Metastable helium induced electron spectroscopy

He* atoms are produced in a two stage cold cathode gas discharge from MFS (Clausthal-Zellerfeld, Germany). The source produces simultaneously also UV light. When the He* atom (1s2s) approaches the surface two different pathways for de-excitation can occur ⁴. The first mechanism is resonant ionisation (RI) followed by Auger neutralisation (AN). The second mechanism is Auger de-excitation (AD). Both mechanisms are illustrated in Figure S4.



Figure S4: Illustration of resonance ionisation (RI) followed by Auger neutralisation (AN) mechanism (left) and the Auger de-excitation (AD) mechanism (right).

The RI/AN mechanism is illustrated on the left side of Figure S4. If the work function of surface is sufficiently low the 2s electron from the He* will undergo resonance ionisation between the surface (unoccupied states) and He* resulting in a positive helium ion. In a second step an electron from the surface may fill the 1s orbital neutralising the helium ion. This process is known as Auger neutralisation. The energy difference between the state from which the electron transfers (Φ_i) to the He ion and the He 1s level is transferred to another electron (at level Φ_i) of the substrate which then results in the emission of this electron from substrate. The sum of the energy of the emitted electron and the electron tunnelling into the He1s state is conserved. A range of combinations of energy levels Φ_i and Φ_i is possible and leads to a broadening of the features in the spectra based on the RI/AN process. The resonance ionisation process is hindered in case of medium to high work function materials and for nonmetallic samples. In this case an alternative process, AD, occurs which is illustrated on the right side of Figure S4. An electron is tunnelling from the substrate into the He 1s level and the energy difference is transferred to the 2s electron in the He atom leading to the emission of an electron from the He*. The AD process results in sharper features in the MIE spectra compared with spectra based on the RI and AN process. Any measurement of MIES will be a combination of all these processes. Depending on the nature of the sample it may be dominated by either RI and AN or AD.

Investigating of materials with a low energy cut-off of the valence electron band can be difficult. An example is C sp² hybridised material. Applying MIES to this material is complicated by the fact that the spectra show contributions from both the RI/AN and AD de-excitation mechanisms. Morgner⁵ has previously investigated the electronic nature of HOPG surfaces with MIES and reported that throughout a range of temperatures the contribution of both deexcitation mechanisms to the overall spectra are changing with the sample temperature. This effect can be used to separate the spectral components related to both de-excitation mechanisms. Spectra resulting from the AD mechanism are rather featureless. This can also been seen in the MIE spectra shown in Figure S5. It is thus concluded that the He^{*} interact with the monolayer MoS_2 via the AD mechanism.



Figure S5: all MIE spectra, they are featureless and thus not meaningful here.

References

- 1. X. Yang and B. Li, *Nanophotonics*, 2020, **9**, 1557-1577.
- 2. C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone and S. Ryu, *ACS Nano*, 2010, **4**, 2695-2700.
- 3. S. Mignuzzi, A. J. Pollard, N. Bonini, B. Brennan, I. S. Gilmore, M. A. Pimenta, D. Richards and D. Roy, *Physical Review B*, 2015, **91**, 195411.
- 4. H. D. Hagstrum, *Physical Review Letters*, 1979, **43**, 1050-1053.
- 5. H. Morgner, in *Physics of Electronic and Atomic Collisions*, eds. Y. Itikawa, K. Okuno, H. TanakaA, A. Yagishita and M. Matsuzawa, 2000, vol. 500, pp. 687-698.