Supplementary Information: Electronic Structure and Enhanced Charge-Density Wave Order of Monolayer VSe_2

Jiagui Feng,[1,2,*] Deepnarayan Biswas,[1,*] Akhil Rajan,[1,*] Matthew D. Watson,[1] Federico Mazzola,[1] Oliver J. Clark,[1] Kaycee Underwood,[1] Igor Marković,[1,3] Martin McLaren,[1] Andrew Hunter,[1] David M. Burn,[4] Liam B. Duffy,[5,6] Sourabh Barua,[7,†] Geetha Balakrishnan,[7] François Bertran,[8] Patrick Le Fèvre,[8] Timur K. Kim,[9] Gerrit van der Laan,[4] Thorsten Hesjedal,[5] Peter Wahl,[1] and Phil D. C. King[1,‡]

[1] *SUPA, School of Physics and Astronomy, University of St. Andrews, St. Andrews KY16 9SS, United Kingdom*

[2] *Suzhou Institute of Nano-Tech. and Nanobionics (SINANO), CAS, 398 Ruoshui Road, SEID, SIP, Suzhou, 215123, China*

[3] *Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Straße 40, 01187 Dresden, Germany*

[4] *Magnetic Spectroscopy Group, Diamond Light Source, Didcot, OX11 0DE, United Kingdom*

[5] *Department of Physics, University of Oxford, Oxford, OX1 3PU, United Kingdom*

[6] *ISIS, STFC, Rutherford Appleton Laboratory, Didcot, OX11 0QX, United Kingdom*

[7] *Department of Physics, University of Warwick, Coventry CV4 7AL, United Kingdom*

[8] *Synchrotron SOLEIL, CNRS-CEA, L'Orme des Merisiers, Saint-Aubin-BP48, 91192 Gif-sur-Yvette, France*

[9] *Diamond Light Source, Harwell Campus, Didcot, OX11 0DE, United Kingdom*

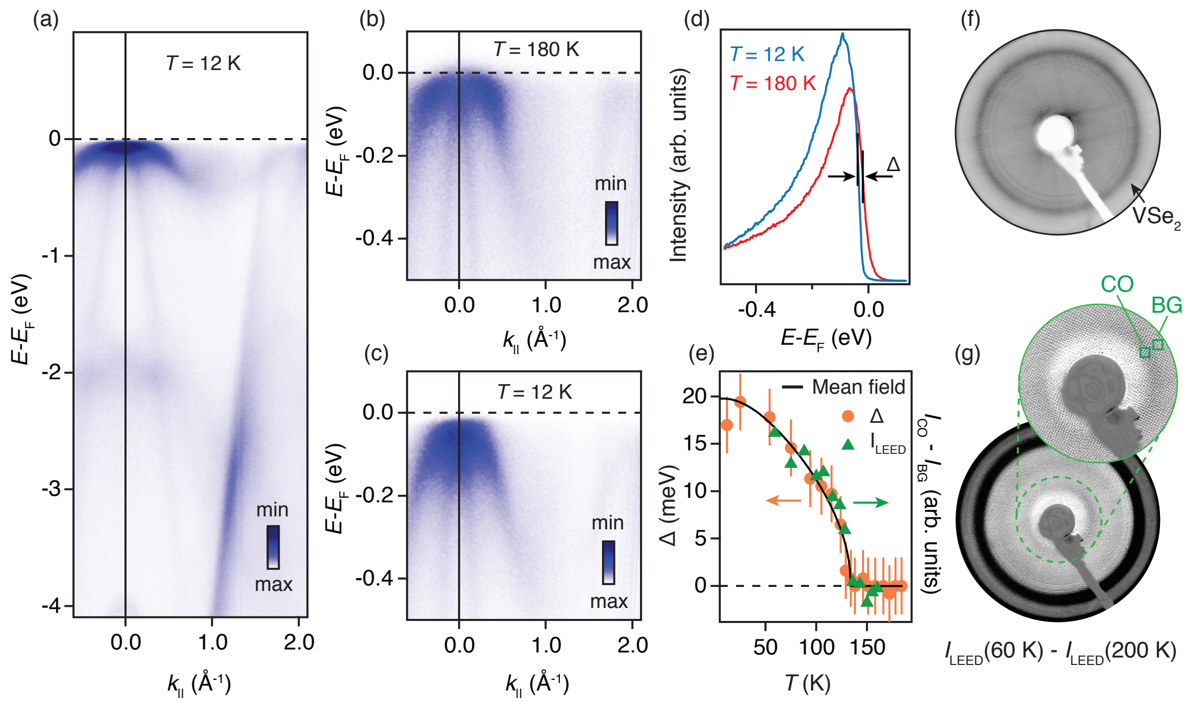

FIG. S1. Charge density wave order in monolayer VSe_2/HOPG. (a) Measured dispersion ($h\nu = 110$ eV). The HOPG substrate contains rotated domains which are smaller than our probing light spot, and so the measured band structure is azimuthally averaged around the Brillouin zone. Nonetheless, relatively sharp band dispersions are still evident close to $\overline{\Gamma}$ where the Se p-derived states are anyway nearly circular, while the angular projection of the remaining states is clearly evident enabling the identification of the V d-derived states as well as the π states of the HOPG. (b,c) Near-E_F measurements indicate a pronounced shifting of the spectral weight away from the Fermi level upon cooling from $T = 180$ K (b) to $T = 12$ K (c). (d) An energy distribution curve (EDC) integrated over the measured angular range, which neglecting matrix element variations approximates to the total density of states, reveal a clear leading-edge midpoint (LEM) shift to higher binding energies by $\sim$20 meV upon cooling, indicative of the opening of a full (or nearly-full) gap in the low-energy electronic structure near E_F. (e) Temperature-dependent opening of this gap, similar to that measured for VSe_2/bilayer graphene discussed in the main text but with a slightly reduced ordering temperature of $T_{\mathrm{CDW}} = 134 \pm 5$ K. (f) Our LEED measurements ($E = 100$ eV, $T = 200$ K) of VSe_2/HOPG show circles due to the random alignment of domains within the probing area. (g) Additional superstructure order can be observed as the emergence of a new circle upon cooling to $T = 60$ K, with a radius consistent with the $\Gamma_{\{11\}}$ Bragg spots of a 4×4 order as for growth on graphene substrates discussed in the main text. The temperature-dependent intensity of the charge-order peaks follows the gap opening observed by ARPES, as shown in (e). We thus conclude that the CDW order is very similar for VSe_2 monolayers grown on both HOPG and bilayer graphene.

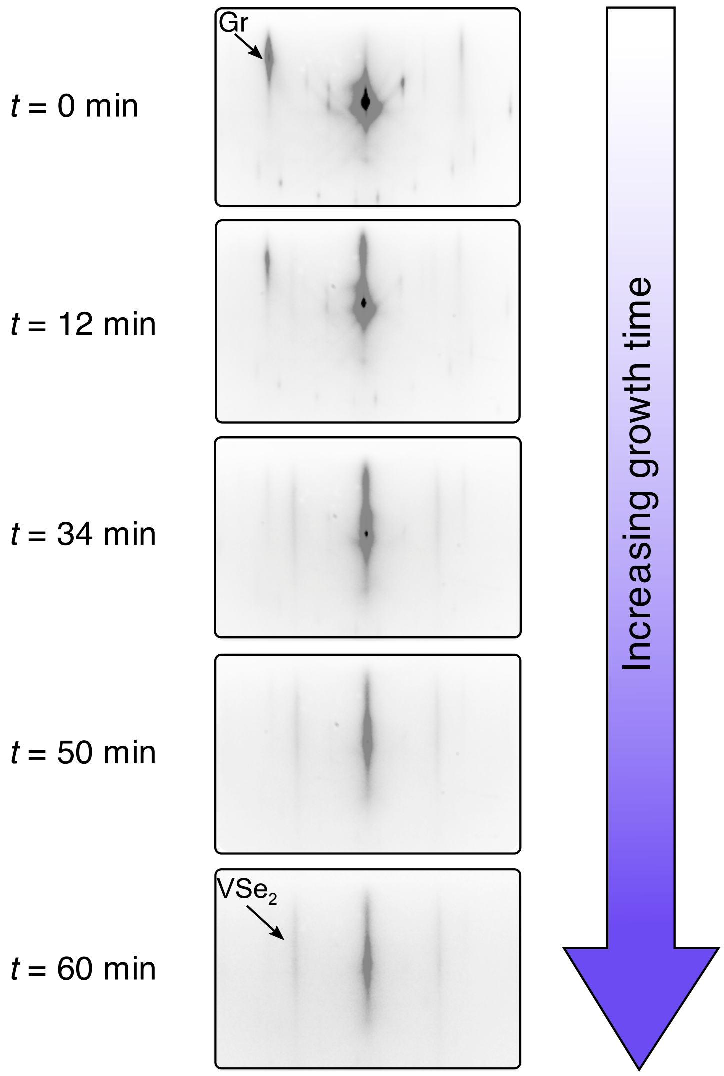

FIG. S2. Monolayer VSe_2 growth. Reflection high-energy electron diffraction measurements as a function of growth time during VSe_2 growth on bilayer graphene/SiC substrates using the method and parameters described in the main text. The substrate RHEED peaks visible at the start of growth are gradually virtually extinguished with increasing growth time, accompanied with the gradual emergence of sharp streaks at smaller spacing from the specular spot which are the Bragg streaks of the VSe_2 layer. This indicates the growth of smooth monolayer films which form in a fully relaxed configuration immediately from the initial stages of the growth, indicating the weak interaction between the grown layer and the underlying substrate.

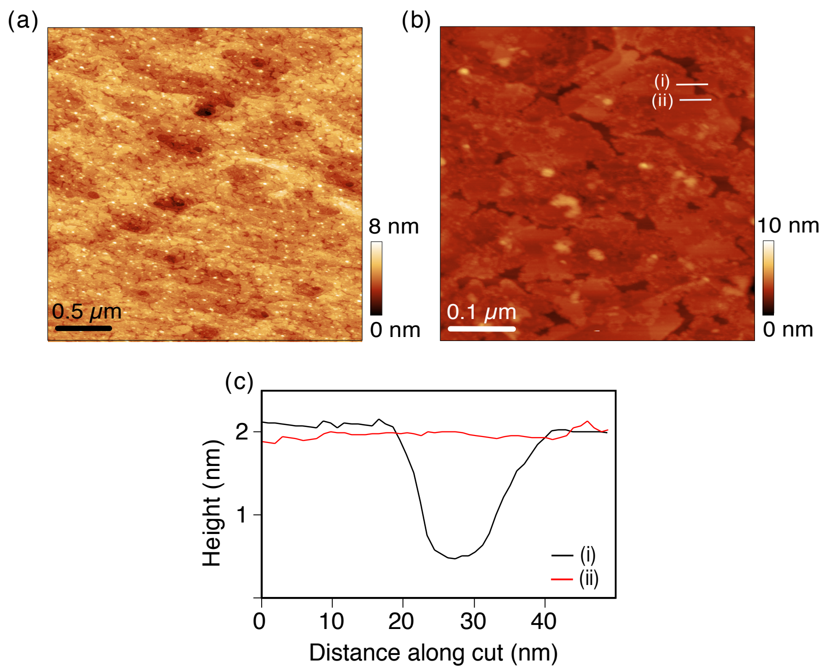

FIG. S3. Surface morphology of MBE-grown monolayer VSe_2. Atomic force microscopy measurements from (a) a 3×3 μm^2 and (b) a 500×500 nm^2 region of VSe_2 grown on a bilayer graphene/SiC substrate. The large-area morphology is relatively rough, reflecting the terraced structure of the underlying graphene layer produced by Si decomposition of SiC by direct current heating in ultra-high vacuum.[1] For smaller areas, however, the AFM measurements indicate the growth of smooth high-quality terraces of VSe_2. This is evident by the low root-mean-squared (rms) roughness along the line profiles shown in (c) for the paths indicated in (b). Moreover, these measurements reveal that the coverage is near-monolayer, with only minimal patches of exposed substrate remaining following the growth, evident as a dark contrast in (b) and a U-shaped dip in the line profile shown in (c), as well as negligible bilayer coverage. The small bright patches visible in (b) are due to residual Se clusters on the surface which are oxidised upon removal of the sample from vacuum. From quantitative analysis of the measured AFM images, we estimate that our typical samples exhibit $>90\%$ monolayer coverage.

* These authors contributed equally

† Current address: Department of Physics, Birla Institute of Technology, Mesra 835215, Ranchi, India

‡ philip.king@st-andrews.ac.uk

[1] Yu, X.; Hwang, C.; Jozwiak, C.; Köhl, A.; Schmid, A.; Lanzara, A. New Synthesis Method for the Growth of Epitaxial Graphene. *J. Electron Spectrosc. Relat. Phenom.* **2011**, *184*, 100–106.