Electronic Supporting Information for:

Layer-Dependent Optical Conductivity in Atomic Thin WS_2 by Reflection Contrast Spectroscopy

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1. SEM analysis of as grown WS_2 islands on SiO_2/Si substrate

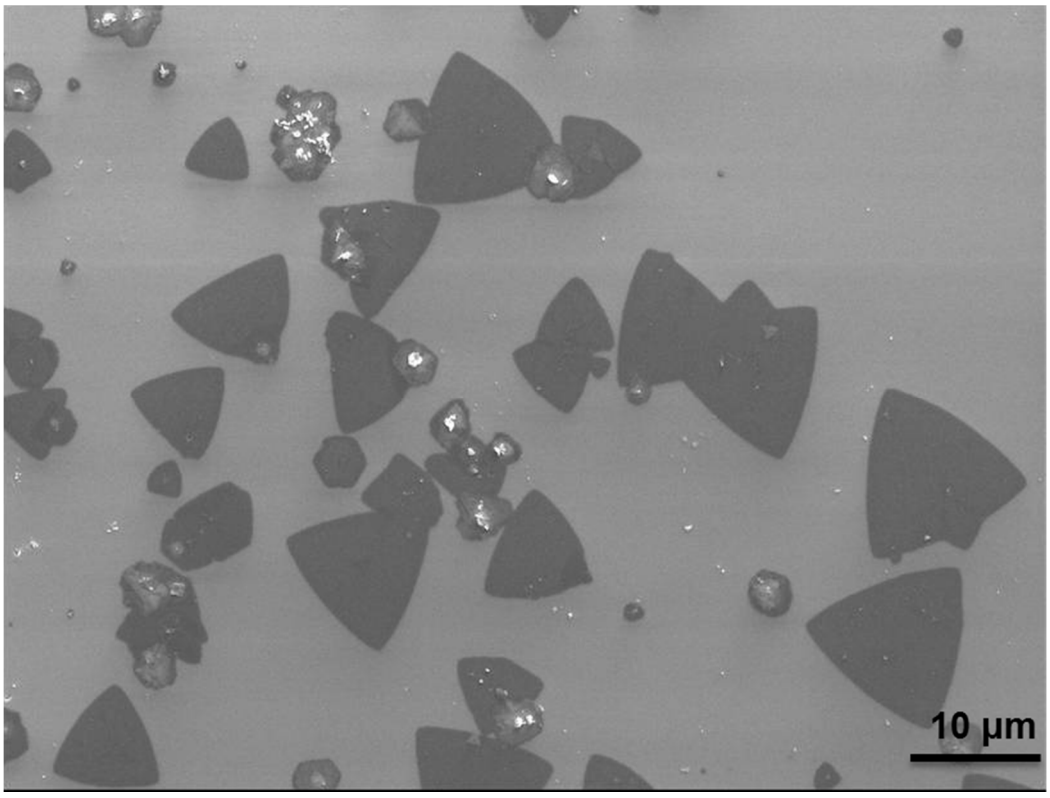

Figure S1. SEM image of as grown WS_2 islands directly on SiO_2/Si substrate by LPCVD. The triangular islands with single contrast correspond to monolayer, whereas the islands containing one, two or more epitaxial layers at their interior with multiple contrasts correspond to bilayer, multilayer and bulk WS_2, respectively.

2. AFM profiles of WS_2 layers

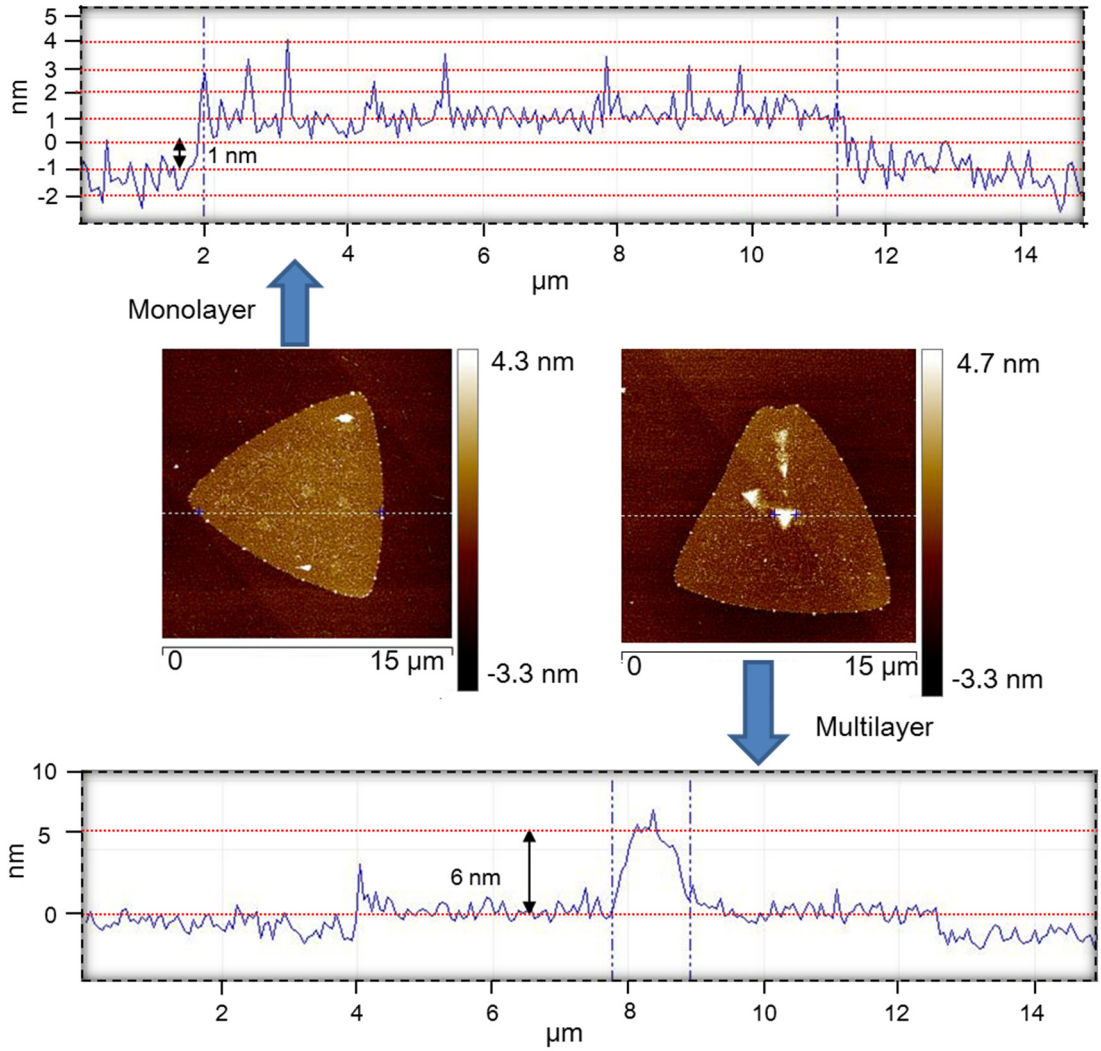

Figure S2. AFM images and height profiles of WS_2 layers. A height of 1 nm and 6 nm in the marked region along y-axis revealing the positions of one and multi WS_2 layers.

3. Electronic band structure calculation using DFT

In order to understand the electronic band structure of the WS_2 layers, the pseudo potential density functional SIESTA package was used for calculations[1-4] with the local density approximation (LDA) representing the exchange correlation potential and with an energy mesh cutoff of 150 Ry. Optimization of initial experimental structures was performed using analytical energy gradient with respect to atomic coordinates and unit cell parameters. We have used a supercell with dimensions equal to the calculated lattice parameters (*a* and *c*) for the band gap calculations of 2H WS_2, however a 13˚A vacuum region was used for the calculations of 1H-WS_2 to isolate the single layer along the *c* axis and ensure no interactions took place between the layers, making it effectively an isolated 2D layer. The Brillouin zone was sampled with a grid of 5×5×1 k-points within the Monkhorst-Pack scheme.[5] Band structures were calculated along the high symmetry points using the path Γ-M-K-Γ.

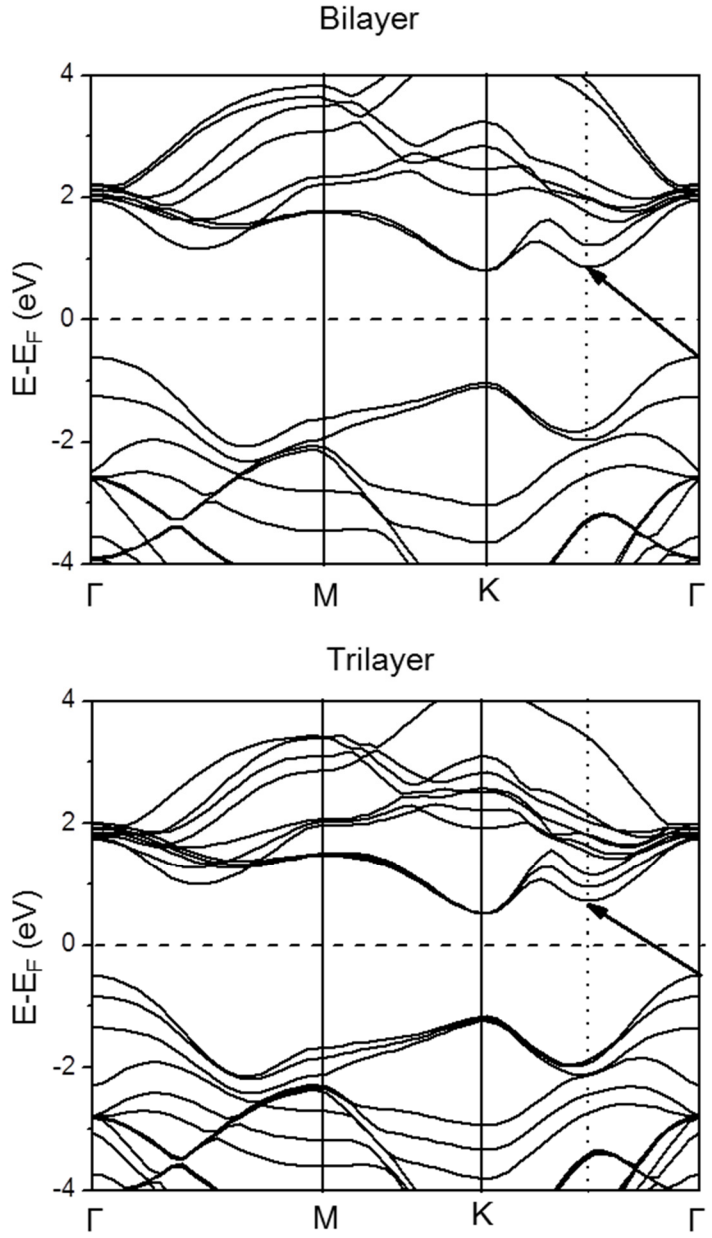

Figure S3. Electronic band structure of bilayer and trilayer WS_2 showing splitting of valence band edge into two and three at K point. The arrow indicates the smallest value of the indirect band gap, which originates from the transition between top of valence band situated at Γ to the bottom of conduction band halfway between Γ and K points. The Fermi level is set at 0 eV.

4. First order derivative of optical conductivity for monolayer WS_2

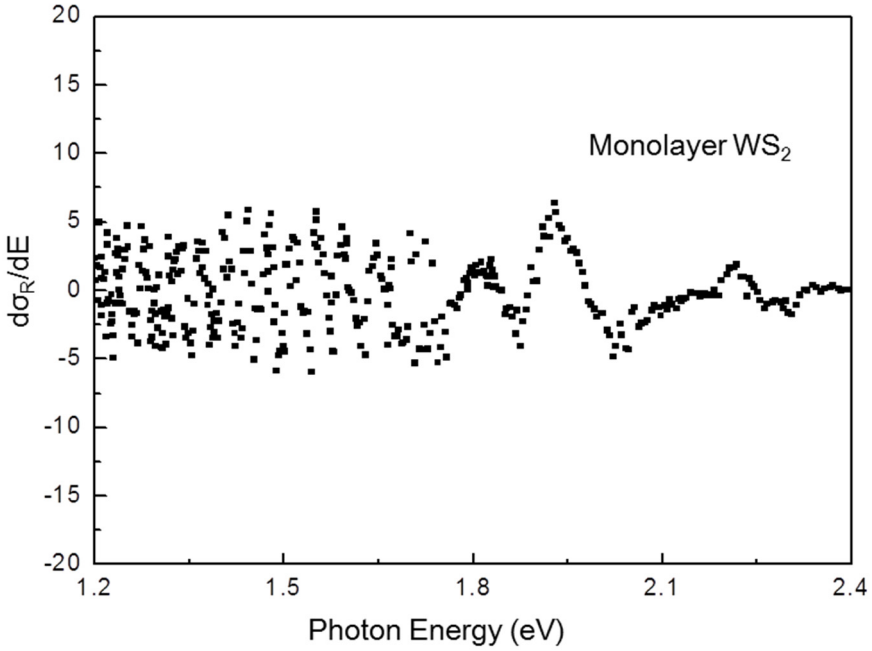

Figure S4. First order derivative of real part of optical conductivity for monolayer WS_2.

5. LPCVD growth of WS_2 films on SiO_2/Si substrates

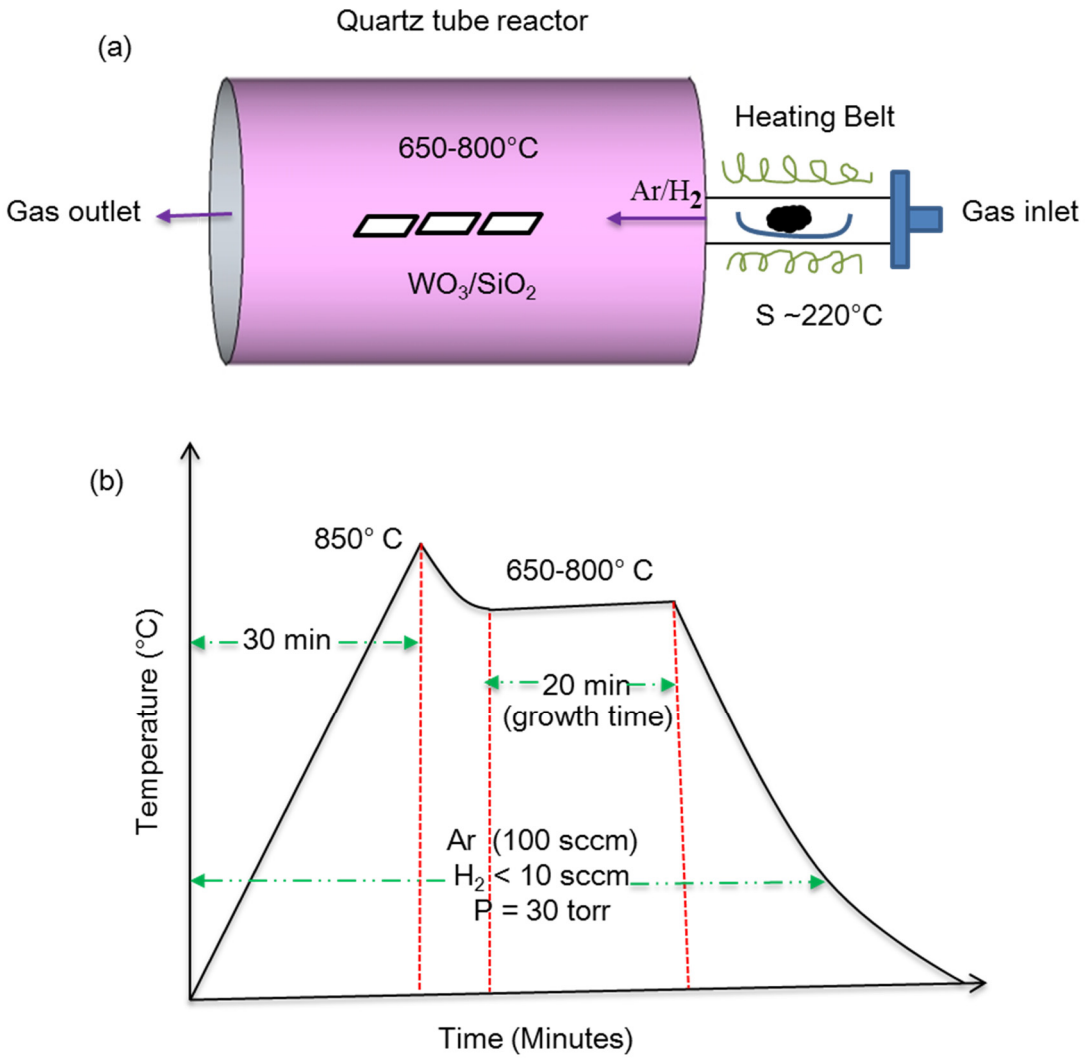

Figure S5 (a) Schematic of the experimental setup used for LPCVD growth of WS_2 films. **(b)** Growth parameters including temperature ramp used for the sulfurization experiments.

References and Notes

(1) Quantum Wise A/S, "Atomistix Tool Kit", **2010**, Ch. 10.8.2.

(2) Brandbyge, M.; Mozos, J.; Ordejon, P.; Taylor, J.; Stokbro, K. Density-Functional Method for Nonequilibrium Electron Transport. *Phys. Rev. B* **2002**, *65,* 165401.

(3) Soler, J. M.; Emilio, A.; Gale, J. D.; Garcia, A.; Junquera, J.; Ordejon, P.; Sanchez-Portal, D. The SIESTA Method for Ab Initio Order-N Materials Simulation. *J. Phys.: Condens. Matter* **2002**, *14,* 2745-2779.

(4) Taylor, J.; Guo, H.; Wang, J. Ab Initio Modeling of Quantum Transport Properties of Molecular Electronic Devices. *Phys. Rev. B* **2001**, *63*, 245407.

(5) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13*, 5188-5192.