Electronic Supplementary Material (ESI) for Nanoscale.

Atomic Structural Catalogue of Defects and Vertical Stacking in 2H/3R Mixed Polytype Multilayer WS_2 Pyramids

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Supporting Information

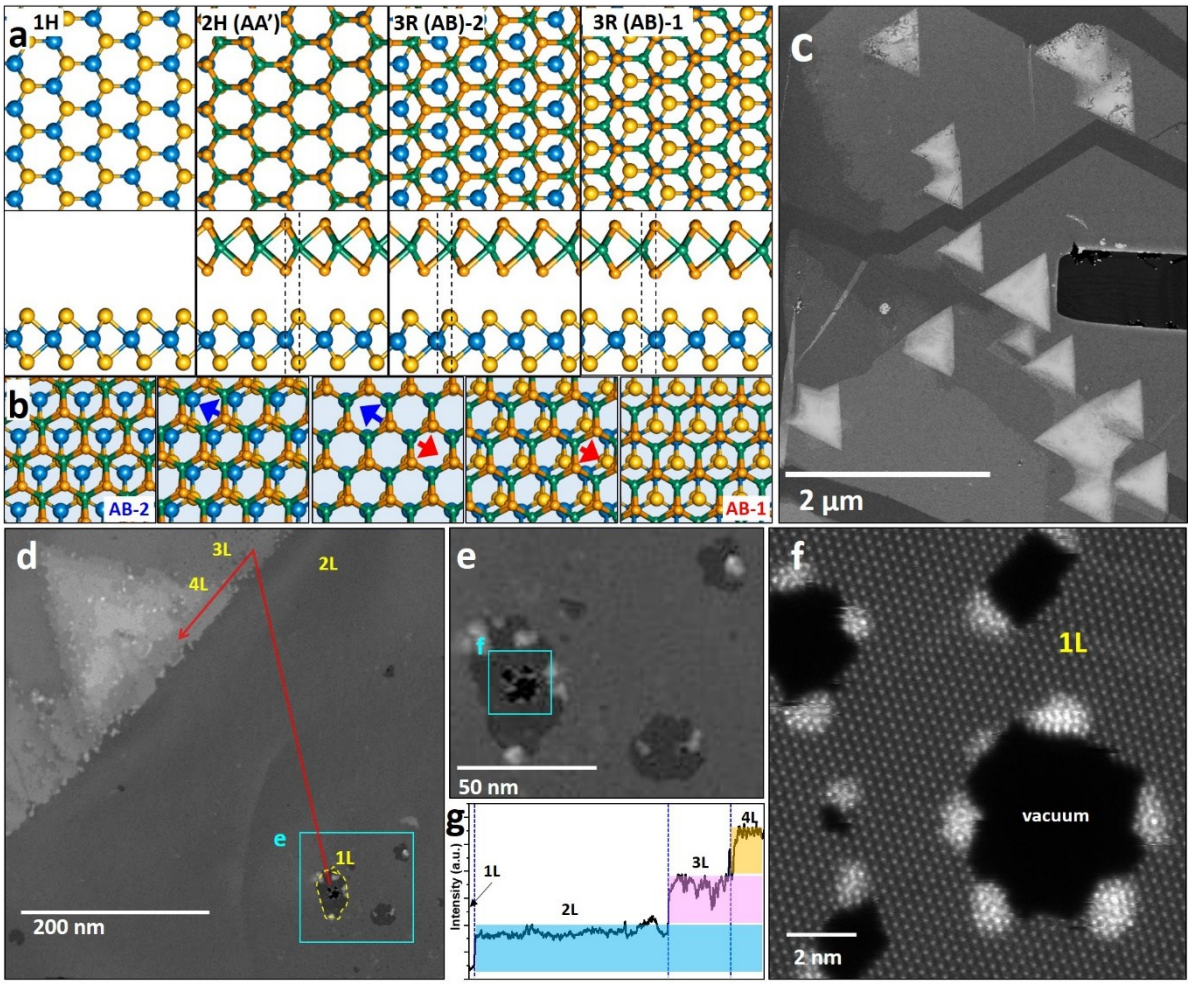


Figure S1. (a) Schematic illustration of stacking order of 2H and 3R with side views. Yellow and orange spheres indicate S atoms and blue and green spheres indicate W atoms in the atomic models. (b) Schematic illustration showing two possible AB structures such AB-1 and AB-2. (c) ADF-STEM image showing multilayer WS_2 pyramids. (d) ADF-STEM image showing the Figure 1(a) as a grey scale. (e) Magnified image of the yellow box in (d). (f) Magnified image of the yellow box in (e), which showing the holes formed by electron beam irradiation and means that this is a monolayer region. (g) Intensity line profile measured from the red arrow in (d) showing the number of layers from monolayer (1L) to quadralayer (4L).

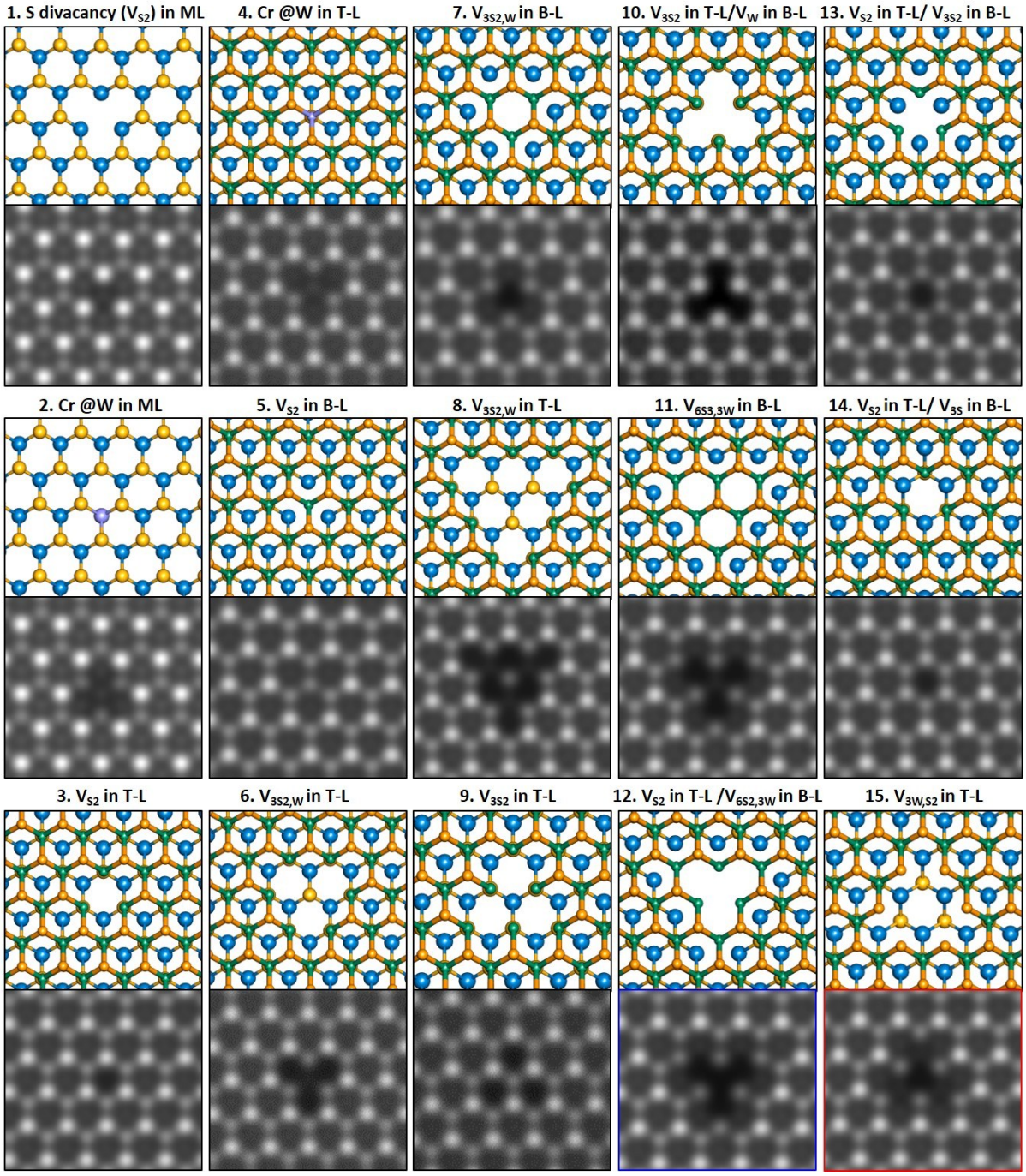


Figure S2. Atomic models and multislice ADF-STEM image simulations corresponding to the all atomic models showing the existing type of pores in AB (AB-1) stacked bilayer WS_2. Yellow and blue spheres indicate S atoms and W atoms in bottom-layer (B-L) and Orange and green spheres indicate S atoms and W atoms in top-layer (T-L) in the atomic models.

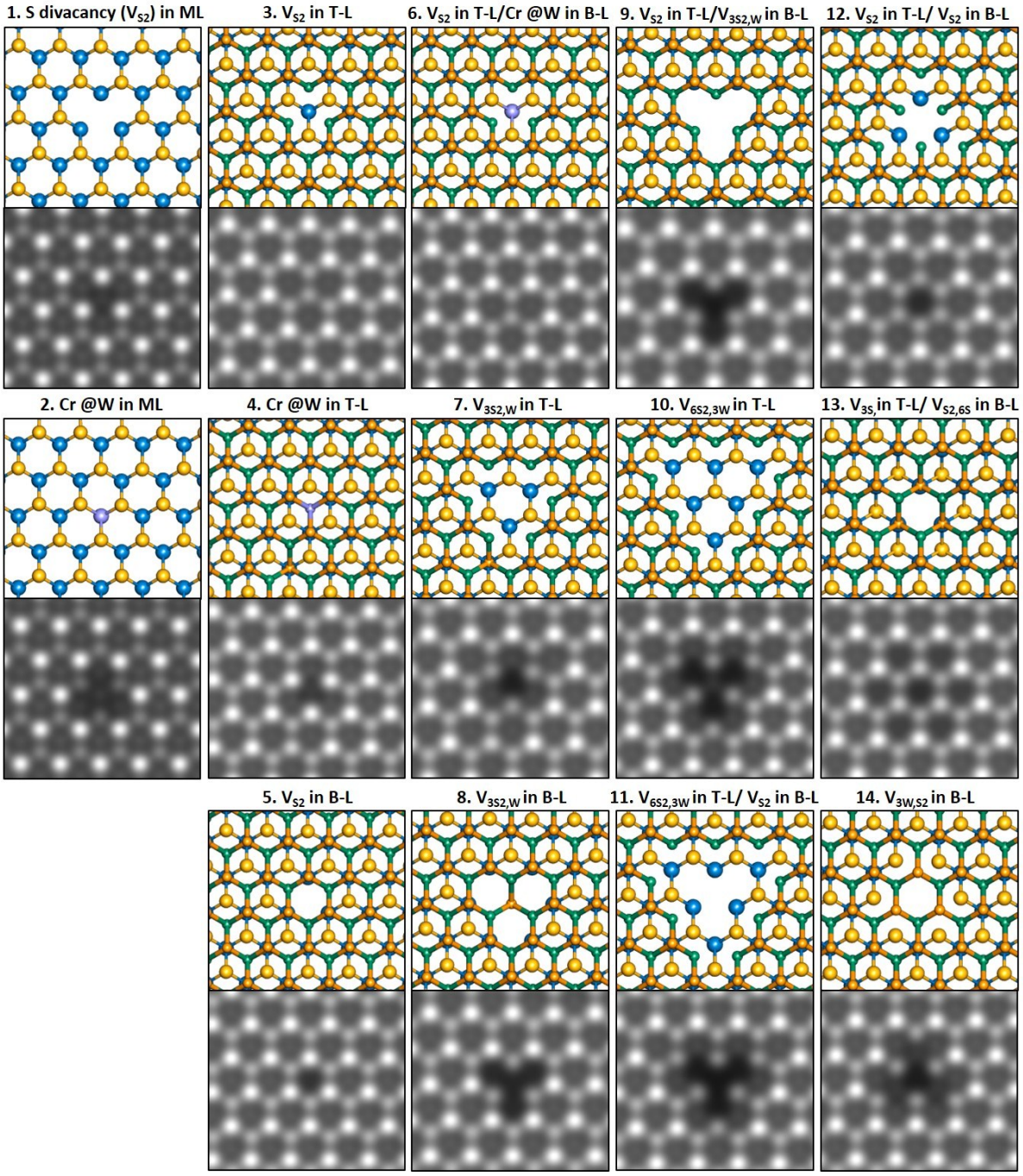


Figure S3. Atomic models and multislice ADF-STEM image simulations corresponding to the all atomic models showing the existing type of pores in AB (AB-2) stacked bilayer WS_2. Yellow and blue spheres indicate S atoms and W atoms in bottom-layer (B-L) and Orange and green spheres indicate S atoms and W atoms in top-layer (T-L) in the atomic models.

Figures S2 and S3 contain Cr-dopant images as No.4 in each images. Based on the previous research[1], those are a single Cr atom substituted at a W site in T-L or B-L. The substitution of a single Cr atom at W positions acted as the substitution at the position of metal atoms in TMDs was clearly reported in our previous paper.[1] So, that is why they were considered as point defects in Figures S2 and S3.

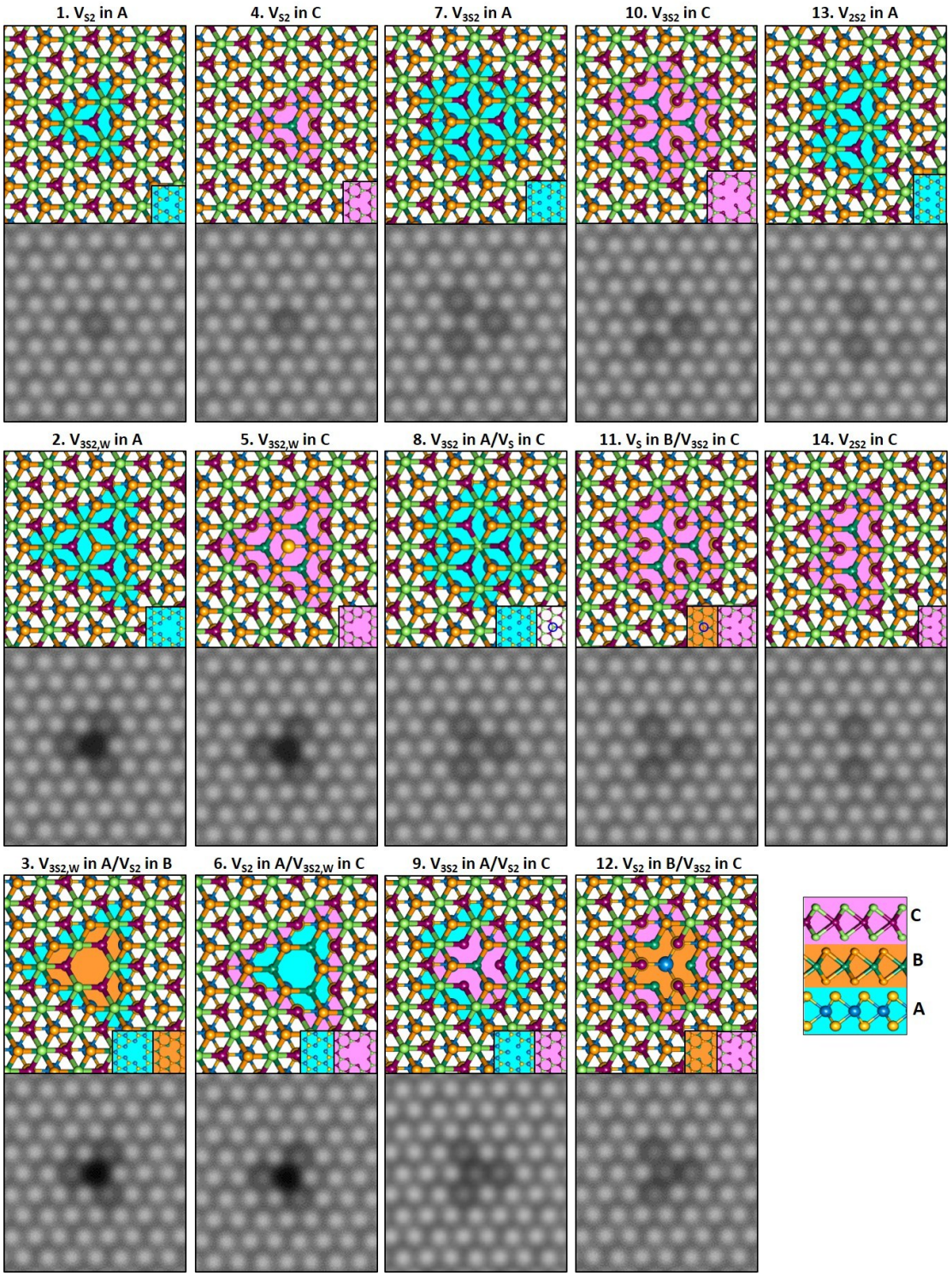
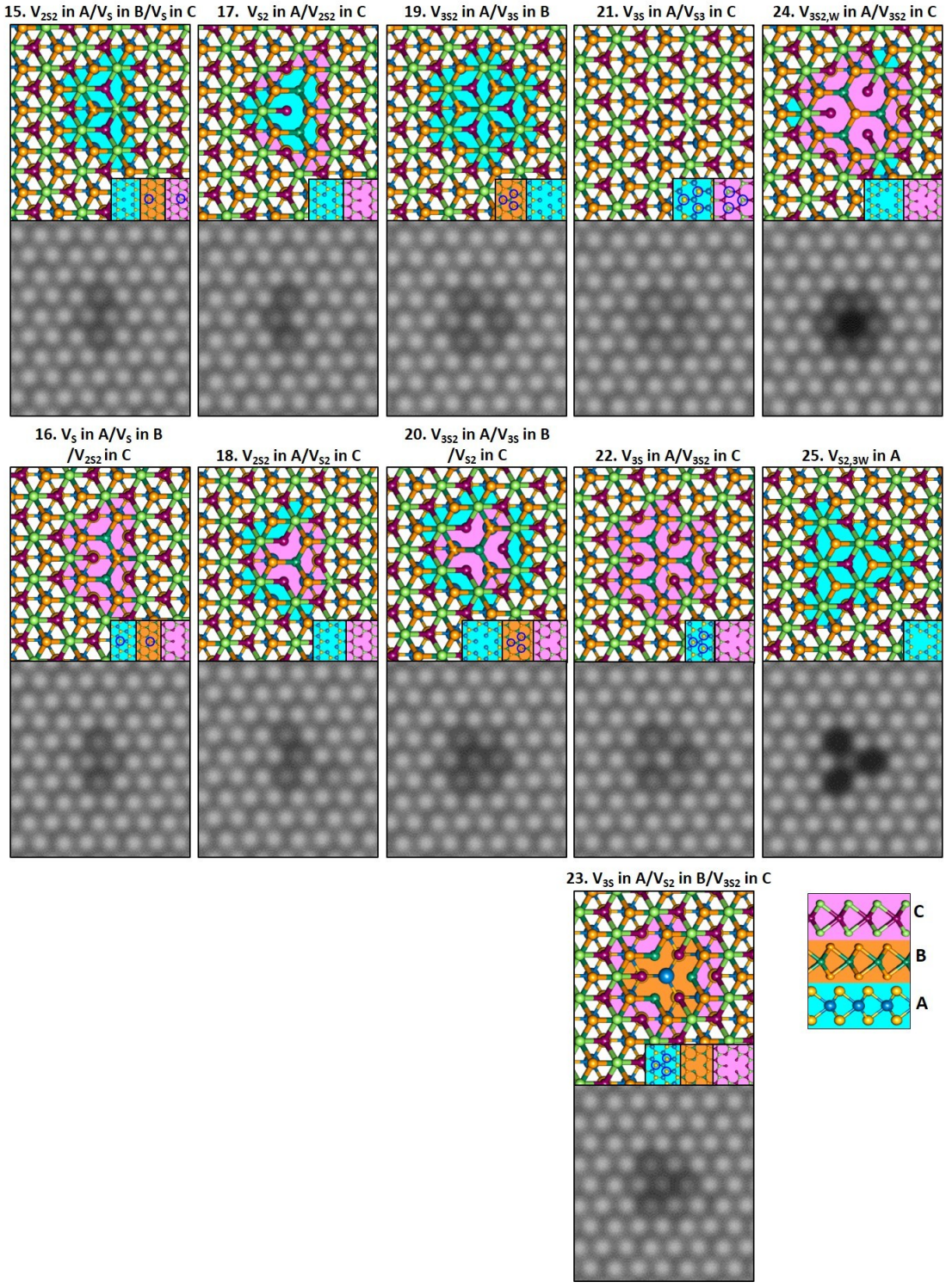


Figure S4. Atomic models and multislice ADF-STEM image simulations corresponding to the

all atomic models showing the existing type of pores in ABC stacked trilayer WS_2. Yellow and

blue spheres indicate S atoms and W atoms in A, coloured by sky-blue. Orange and green

spheres indicate S atoms and W atoms in B, coloured by orange. Green-yellow and purple



spheres are S atoms and W atoms in C, coloured by pink. All insets in the atomic models indicate atomic structures in layers where pores exist. Blue-lined circles in the insets indicate S vacancies.

Figure S5. Atomic models and multislice ADF-STEM image simulations corresponding to the all atomic models showing the existing type of pores in ABC stacked trilayer WS_2, further.

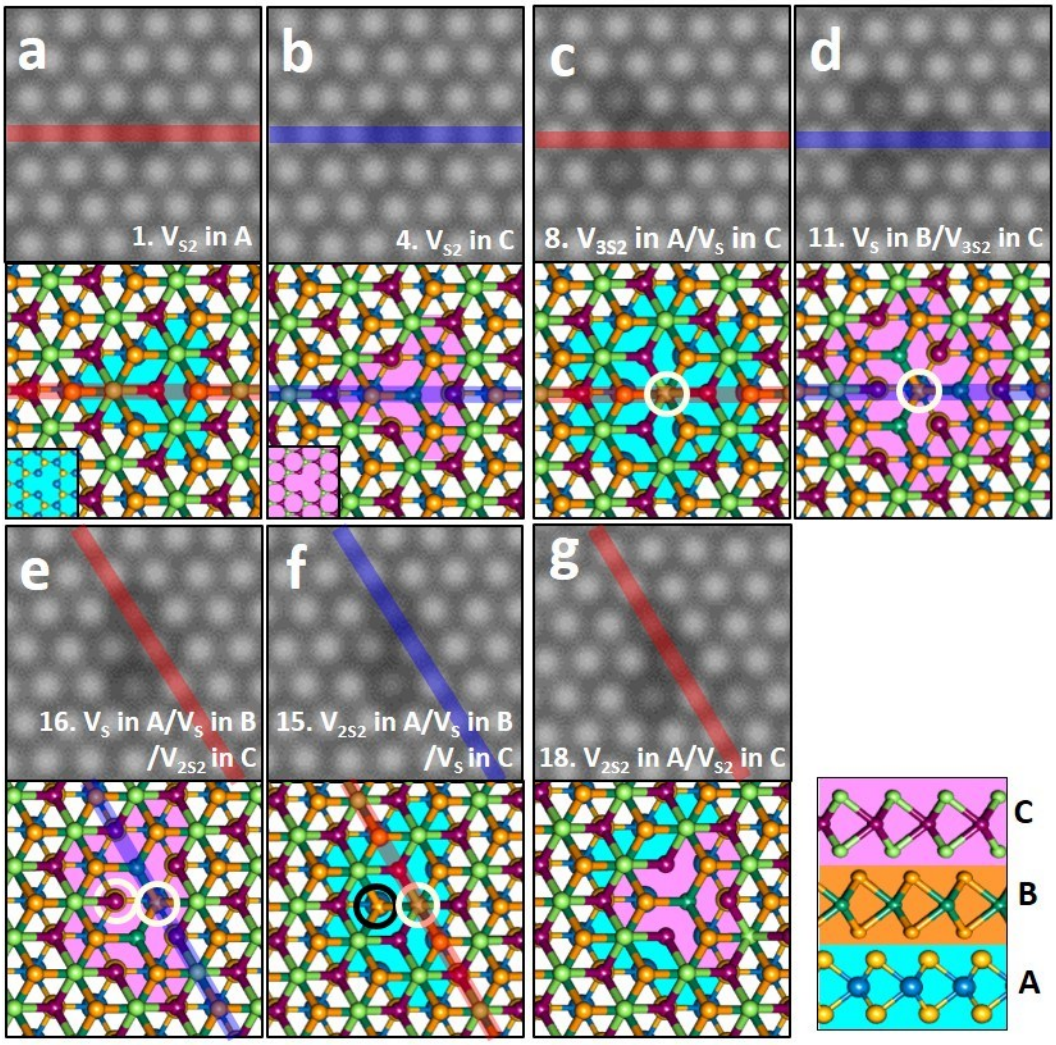


Figure S6. Atomic models and multislice ADF-STEM image simulations corresponding to the all atomic models showing the type of pores in Figure 6. Selected lines (red and blue) indicate the region of measured intensity line profiles in Figure 6. White-lined circles indicate S vacancies and black-lined circle indicates an S vacancy in B.

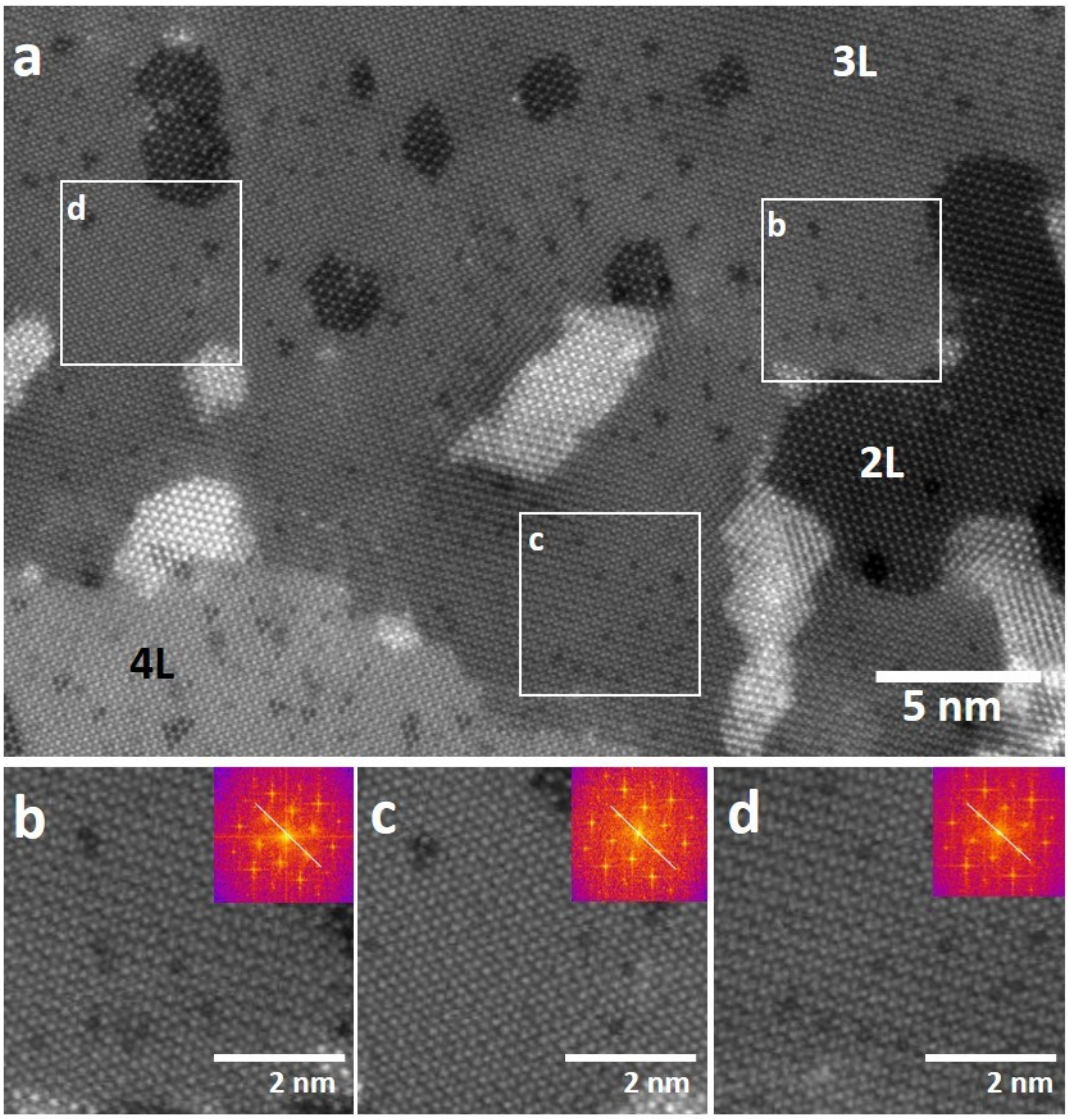


Figure S7. (a) ADF-STEM image showing the trilayer WS_2 with the quadralayer and bilayer. (b,c,d) Magnified images of the white boxes in (a). The insets indicate clear main hexagonal spots which means its layer has periodic stacking order without rotations between each layers.

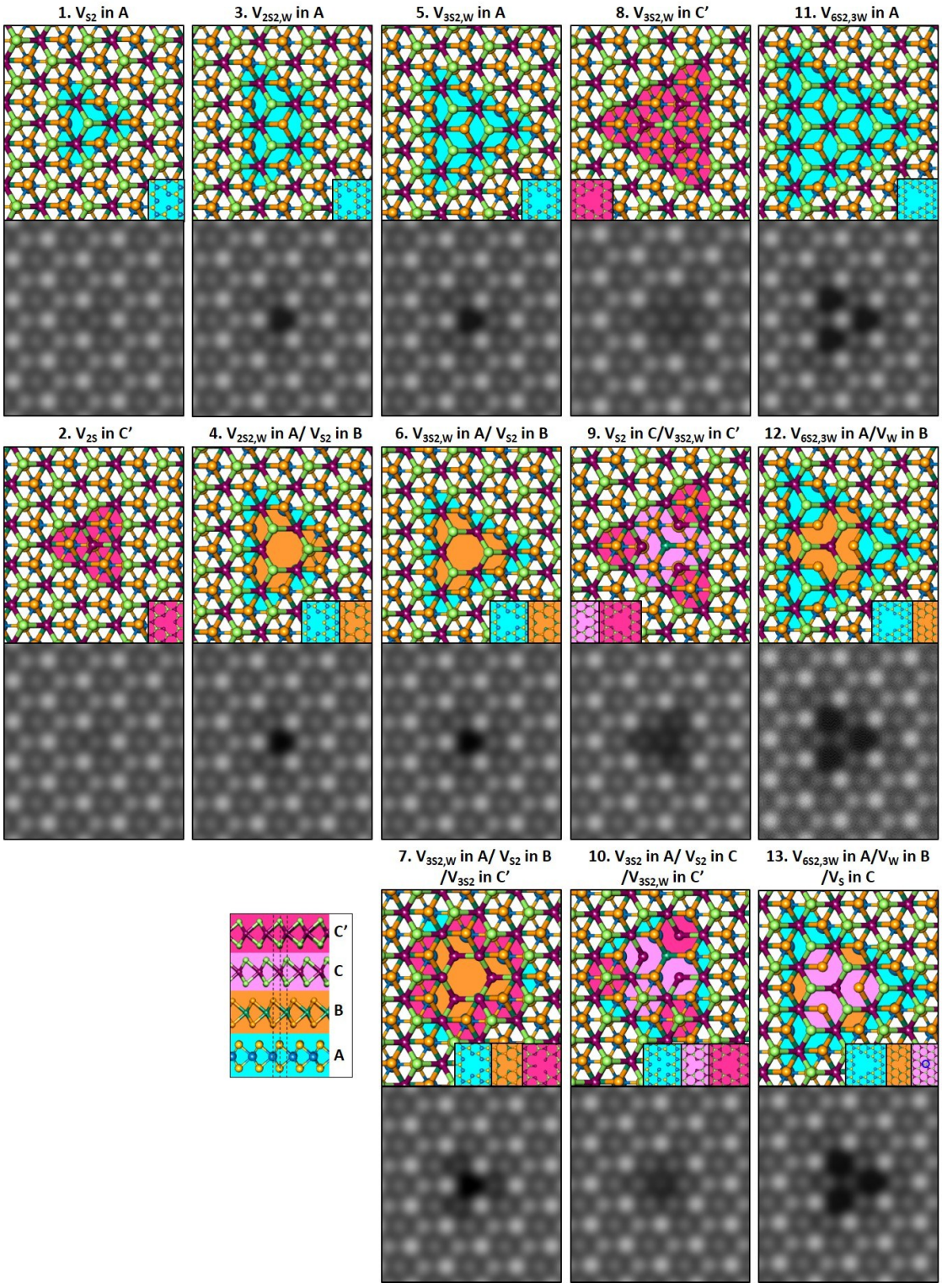


Figure S8. Atomic models and multislice ADF-STEM image simulations corresponding to the all atomic models showing the existing type of pores in ABCC' stacked quadralayer WS_2. Yellow and blue spheres indicate S atoms and W atoms in A, coloured by sky-blue. Orange and green spheres indicate S atoms and W atoms in B, coloured by orange. Green-yellow and purple spheres are S atoms and W atoms in C, coloured by pink, and C', coloured by coral.

CC’ stacked layers have 2H stacking. All insets in the atomic models indicate atomic structures in layers where pores exist. Blue-lined circle in the inset of 13. indicates the S vacancy.

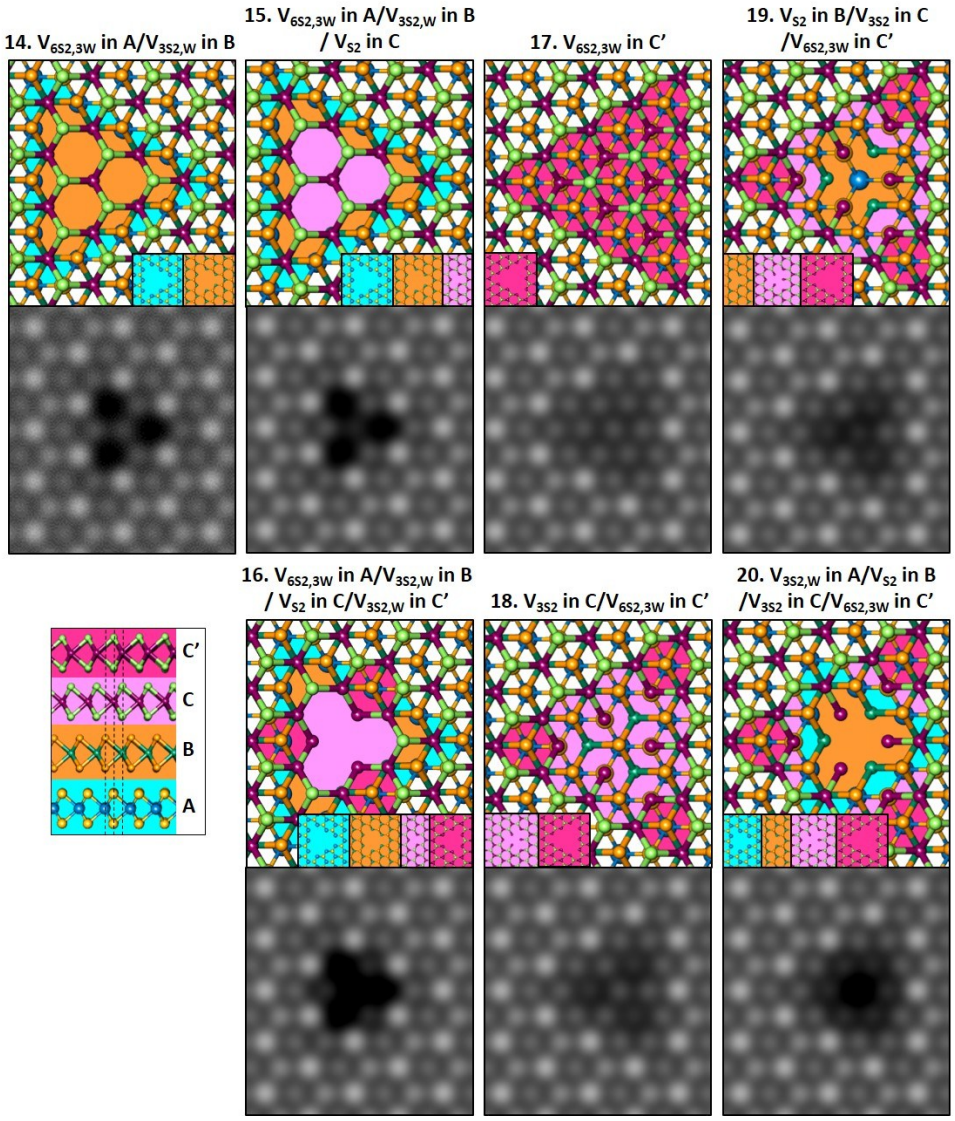


Figure S9. Atomic models and multislice ADF-STEM image simulations corresponding to the all atomic models showing the existing type of pores in ABCC’ stacked quadralayer WS_2, further.

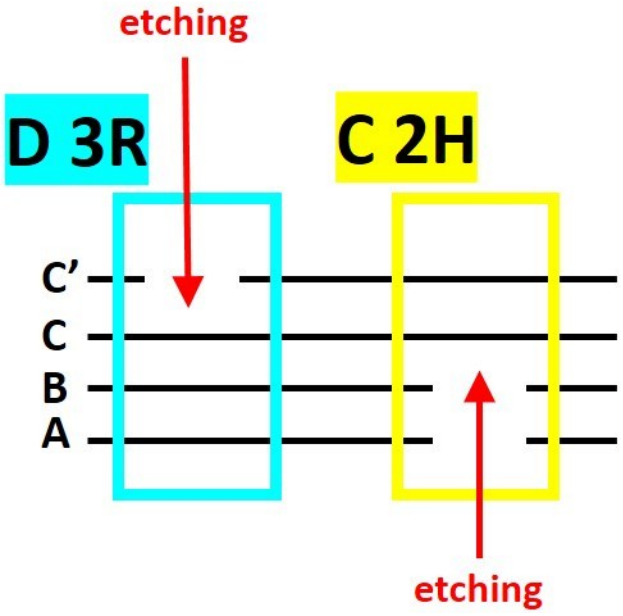


Figure S10. Schematic illustration of formation 3R stacked trilayer and 2H stacked bilayer WS_2 in the quadralayer according to etching directions.

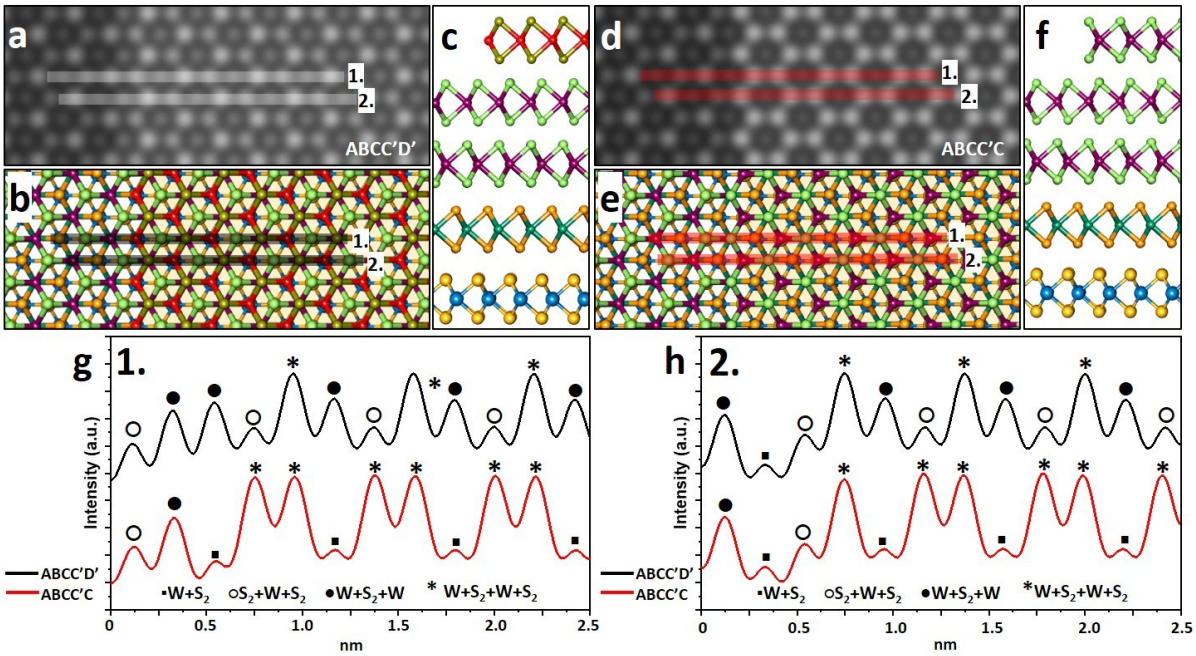


Figure S11. Comparison between ABCC'D' stacked and ABCC'C stacked pentalayers using multislice image simulations (a, d) corresponding to atomic models (b, e) and intensity line profiles (g, h), respectively.

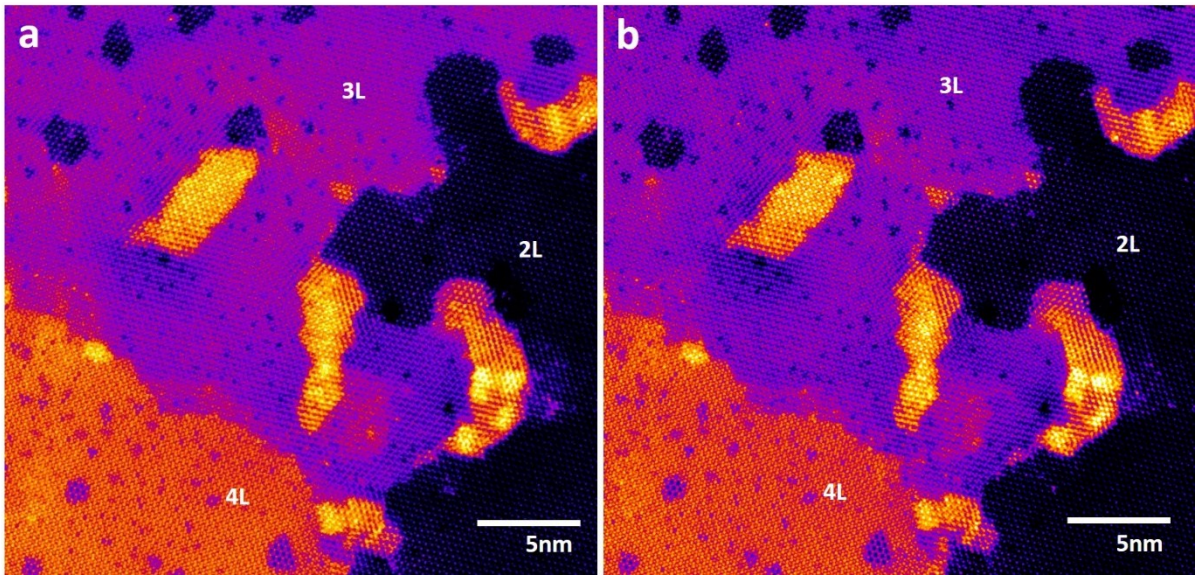


Figure S12. Continuous ADF-STEM image showing that no new defects and radical defect extension by electron beam irradiation for multilayer WS_2 have occurred. The time interval of this continuous image is 4 min 17 sec.

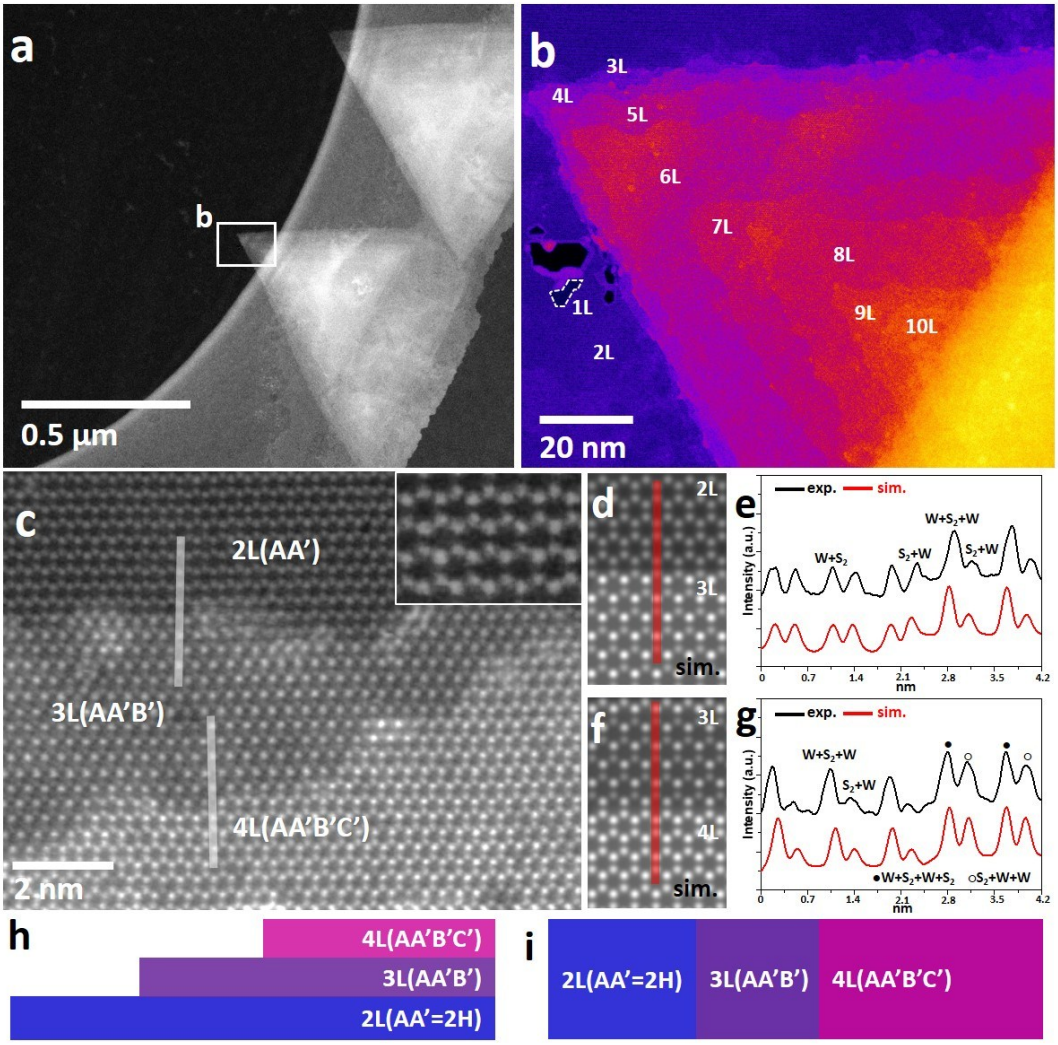


Figure S13. CVD grown WS_2 pyramids with 2H/3R mixed stacking order. (a) ADF-STEM image showing the pyramids. (b) Magnified images from the white box in (a). (c) Edge of the pyramid showing the atomic arrangement from the bilayer to quadralayer with inset showing the atomic arrangement of bilayer having 2H stacking. (d) Multislice ADF-STEM image simulation in the step edge between the bilayer and trilayer. (e) Intensity line profiles measured from the white line indicating the step edge between the bilayer and trilayer in (c) and the red line in (d). (f) Multislice ADF-STEM image simulation in the step edge between the trilayer and quadralayer. (g) Intensity line profiles measured from the white line indicating the step edge between the trilayer and quadralayer in (c) and the red line in (f). (h, i) Illustrations showing the side view and top view of (c).

REFERENCES

1. Robertson, A. W.; Lin, Y.-U.; Wang, S.; Sawada, H.; Allen, C. S.; Chen, Q.; Lee, S.; Lee, G.-D.; Lee, J.; Han, S.; Yoon, E.; Kirkland, A. I.; Kim, H.; Suenaga, K.; Warner, J. H. Atomic Structure and Spectroscopy of Single Metal (Cr, V) Substitutional Dopants in Monolayer MoS_2. ACS Nano 2016, 10, 10227-10236.