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SUPPORTING INFORMATION

Hydrogen-assisted Step-edge Nucleation of $MoSe_2$ monolayers on Sapphire Substrate

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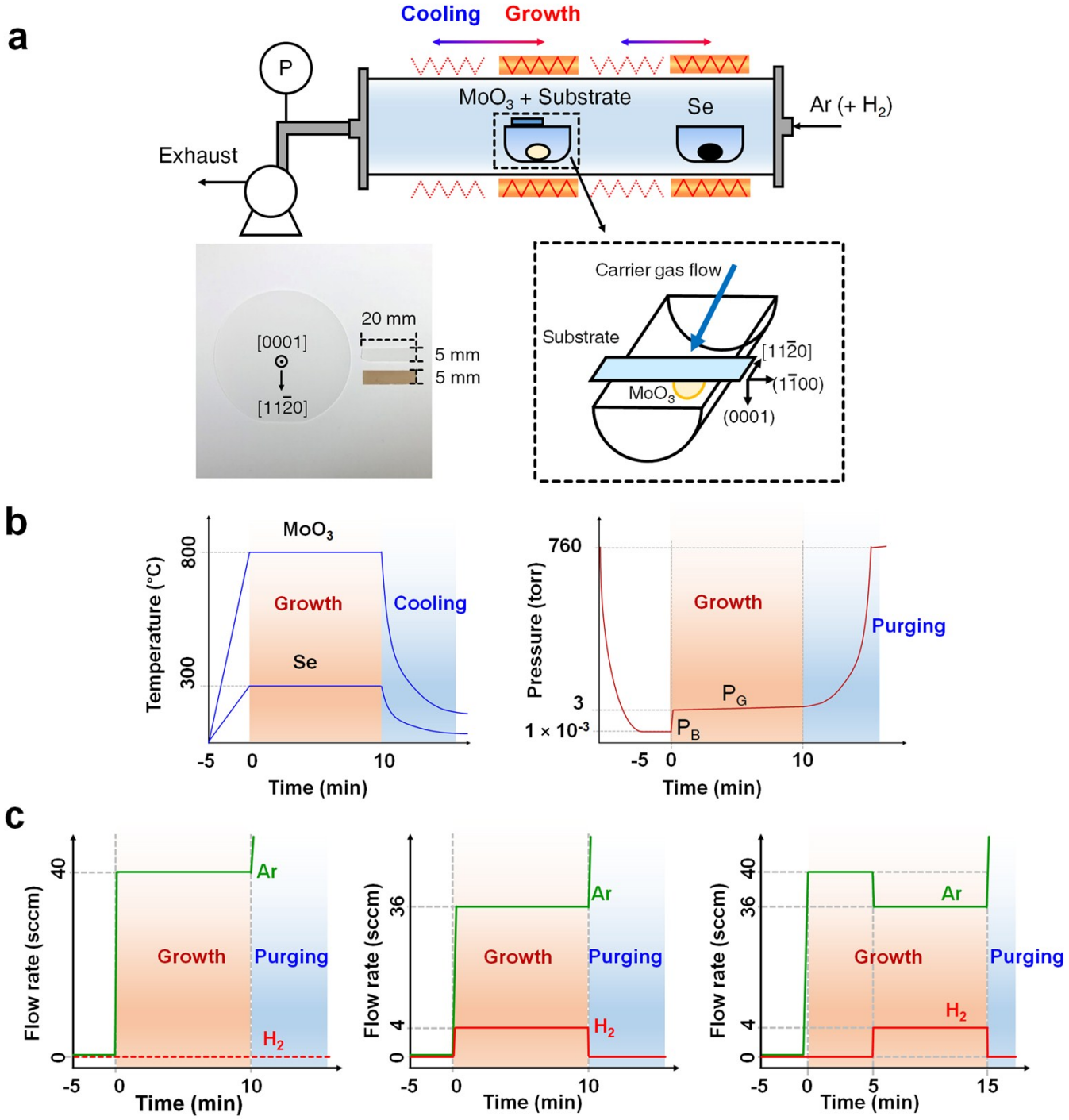

Figure S1. (a) Schematic diagram of the LPCVD system used in this study with a photograph of a 2" diameter sapphire wafer and representative substrates (5mm × 20 mm) before and after $MoSe_2$ growth. Geometry of the substrate orientation relative to the gas flow is highlighted in a dotted box. **(b)** Precursor temperature and system pressure profiles as a function of growth time. **(c)** Pressure and temperature profiles as a function of time during $MoSe_2$ growth, corresponding to Figure 1.

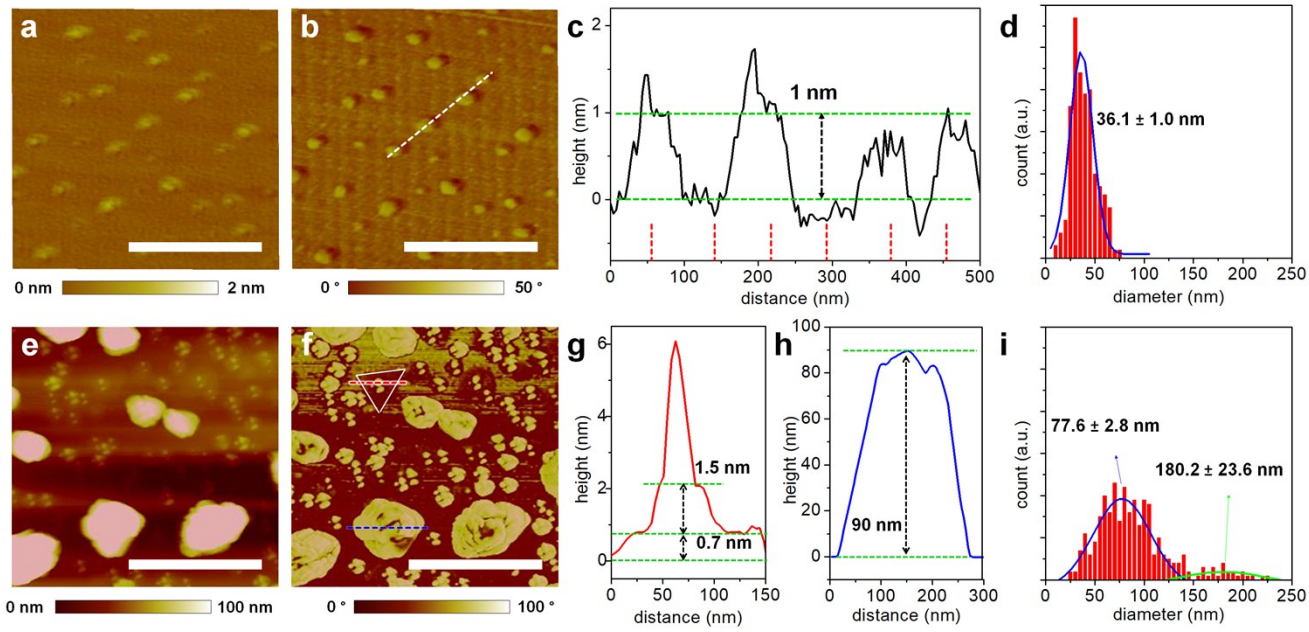

Figure S2. AFM characterization of samples grown under various H_2 introduction conditions. **(a, b)** AFM height and phase image of MoO_3 nanoparticles corresponding to Figure 1a. Scale bars, 500 nm. **(c)** Height profile of a white dotted line shown in (b). **(d)** Size distribution of particles measured from Figure 1a. **(e, f)** AFM height and phase image of $MoSe_2$ domains corresponding to Figure 1b. Scale bars, 500 nm. **(g, h)** Height profiles of red and blue dotted lines shown in (f). **(i)** Size distribution of $MoSe_2$ domains measured from Figure 1b.

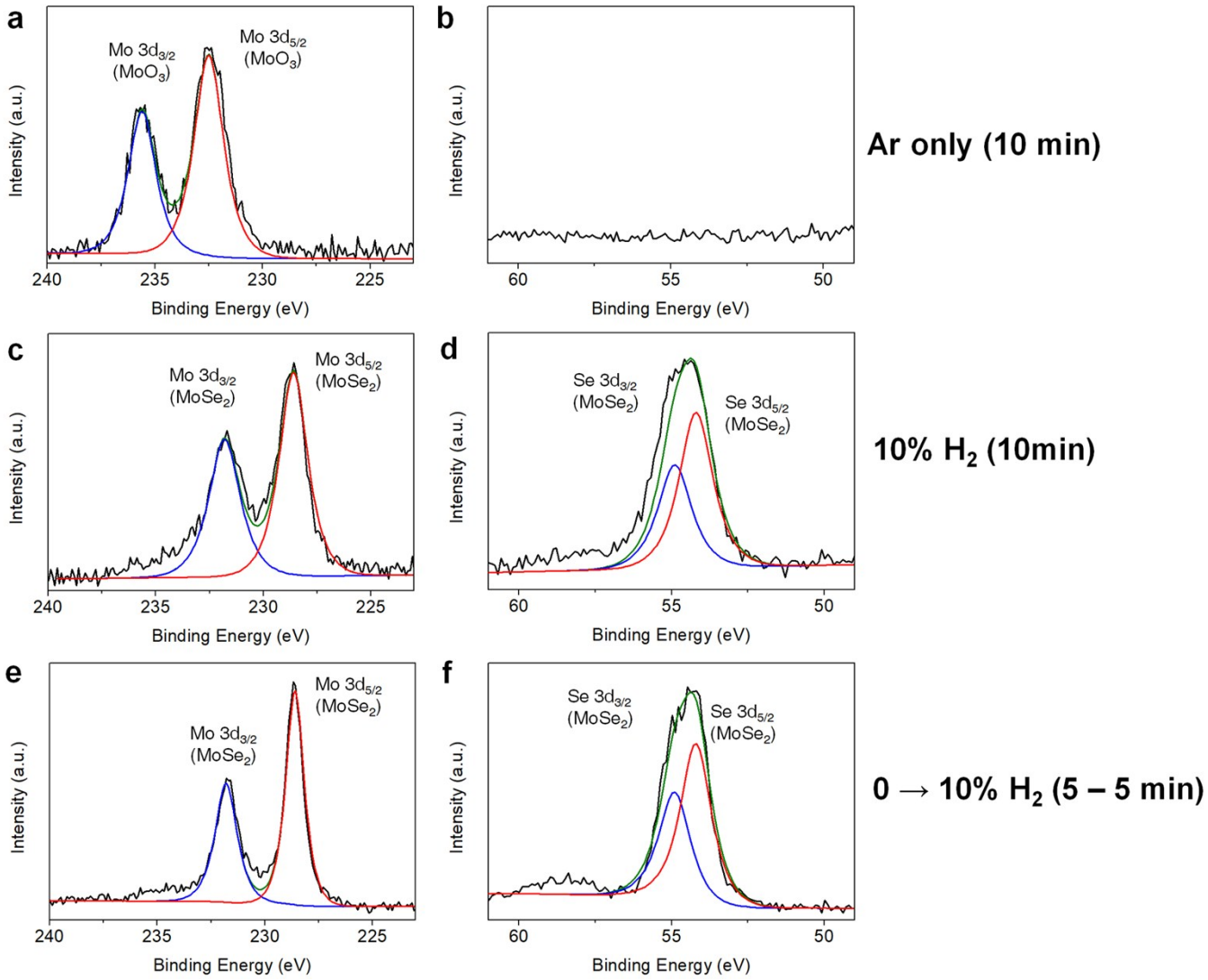

Figure S3. XPS spectra of $MoSe_2$ grown at 750℃. Core-level spectra of Mo 3d and Se 3d obtained from; **(a, b)** Ar only (10 min), **(c, d)** 10 % H_2 (10 min), and **(e, f)** 0 → 10% H_2 (5 – 5 min). The peaks observed at 235.6 and 232.5 eV in (a) correspond to MoO_3. Note that Se is not observed in (b). The peaks at 231.8 and 228.6 eV in (c), (e) correspond to Mo of $MoSe_2$ and those at 54.9 and 54.2 eV in (d), (f) correspond to Se of $MoSe_2$. The quantitative analysis based on the integrated Mo 3d and Se 3d peak intensity indicates the ratio of Se to Mo is 1.17 for 10% H_2 (10 min) and 1.39 for 0 → 10% H_2 (5 – 5 min), respectively. The discrepancy to the theoretical ratio of 1:2 is attributed to Se defects generation induced by the H_2 introduction.

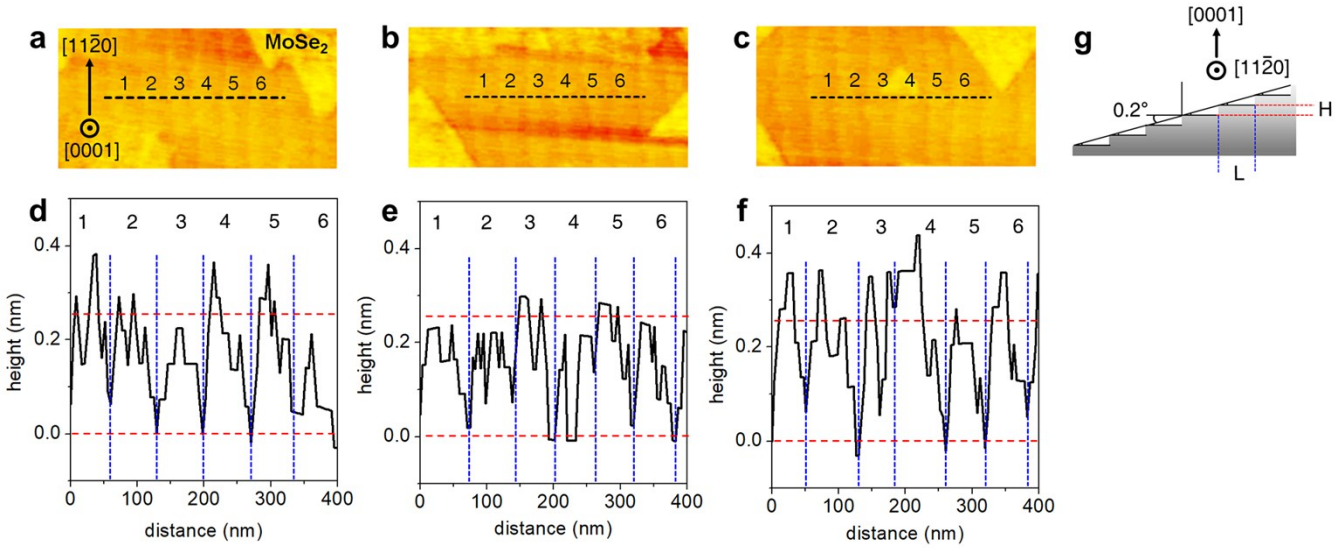

Figure S4. Step height-profile analysis and substrate orientation. **(a, b, c)** AFM height image of Al_2O_3 surface that the step is along (11$\bar{2}$0). Scale bars, 100 nm. **(d, e, f)** Height profile measured from the black dashed line in (a, b, c). The step height and terrace width range from 0.2 to 0.3 nm and from 60 to 70 nm, respectively, corresponding to Al or O steps of sapphire (0001) surface with a miscut angle of 0.2 °. **(g)** Schematic drawing showing the relationship between the miscut angle and step height/terrace width.

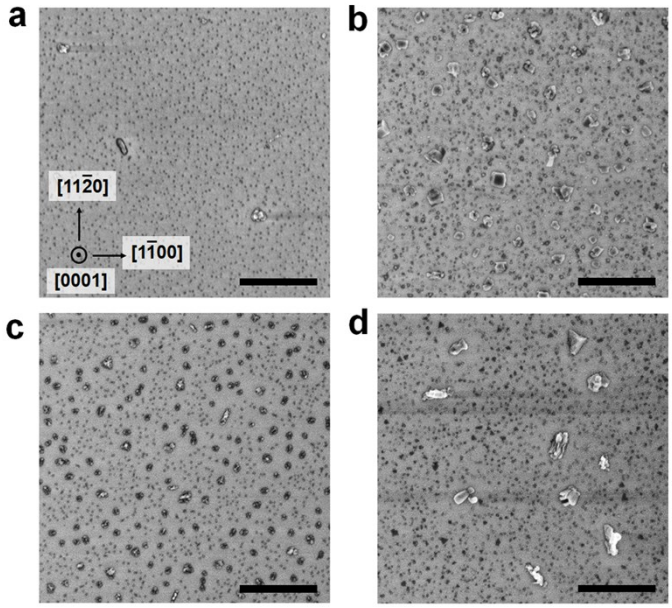

Figure S5. SEM images of the samples grown with simultaneous H_2 flow with Ar from the beginning of growth; **(a)** 10 % H_2 (5 min), **(b)** 10 % H_2 (10 min), **(c)** 20 % H_2 (5 min), and **(d)** 20 % H_2 (10 min). Scale bars, 1μm. The growth temperature is 750 ℃.

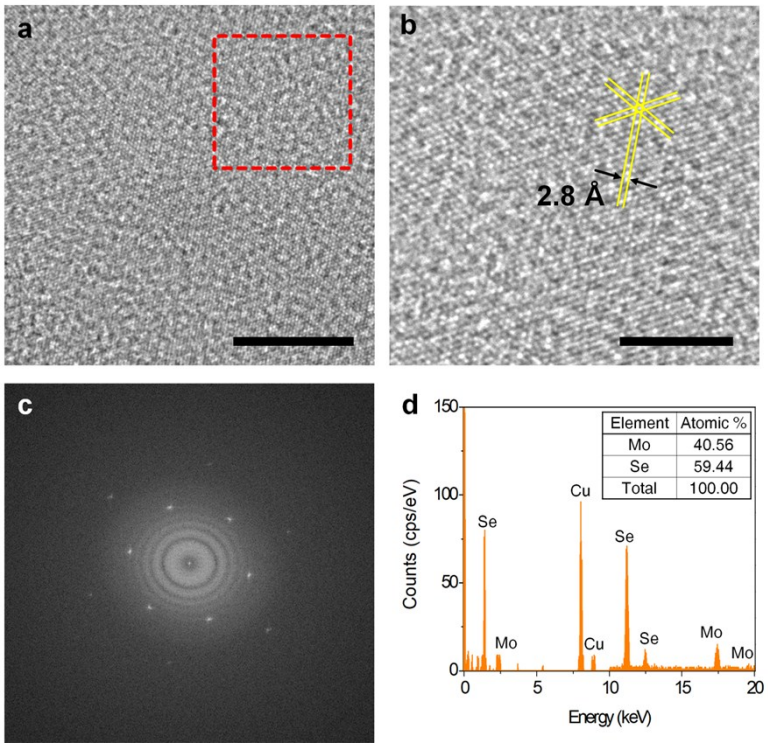

Figure S6. **(a)** HRTEM image of $MoSe_2$ monolayers obtained from the condition of 0 → 10% H_2 (5 – 10 min), PMMA – transferred onto a TEM grid. Scale bar, 10 nm. **(b)** Magnified image of the red dotted box in (a). The spacing between the lattice fringes is 2.8 Å, which corresponds to $MoSe_2$ (100). Scale bar, 5 nm. **(c)** Fast Fourier Transform (FFT) patterns measured from (a) revealing single crystalline nature of grown $MoSe_2$ monolayers. **(d)** EDX spectra of the $MoSe_2$ from (a). The calculated stoichiometry based on the spectra shows that Mo to Se ratio is 1.46, well corresponding to the XPS analysis in Figure S3.

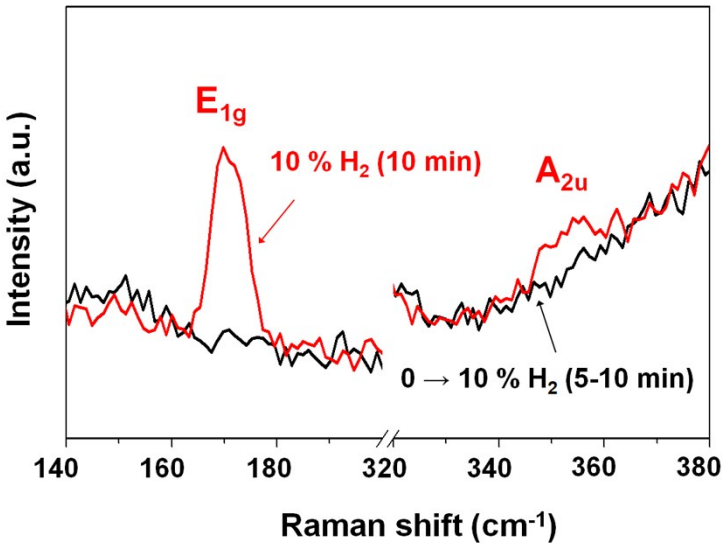

Figure S7. Comparison of the Raman spectra of $MoSe_2$ grown with 10% H_2 (10 min) (red) and 0 → 10% H_2 (5 – 10 min) (black) at 750 ℃. E_{1g} (169 cm^{-1}) and A_{2u} (354 cm^{-1}) modes corresponding to bulk/few-layer $MoSe_2$ are observed under the condition of simultaneous introduction, but not from the delayed introduction condition.

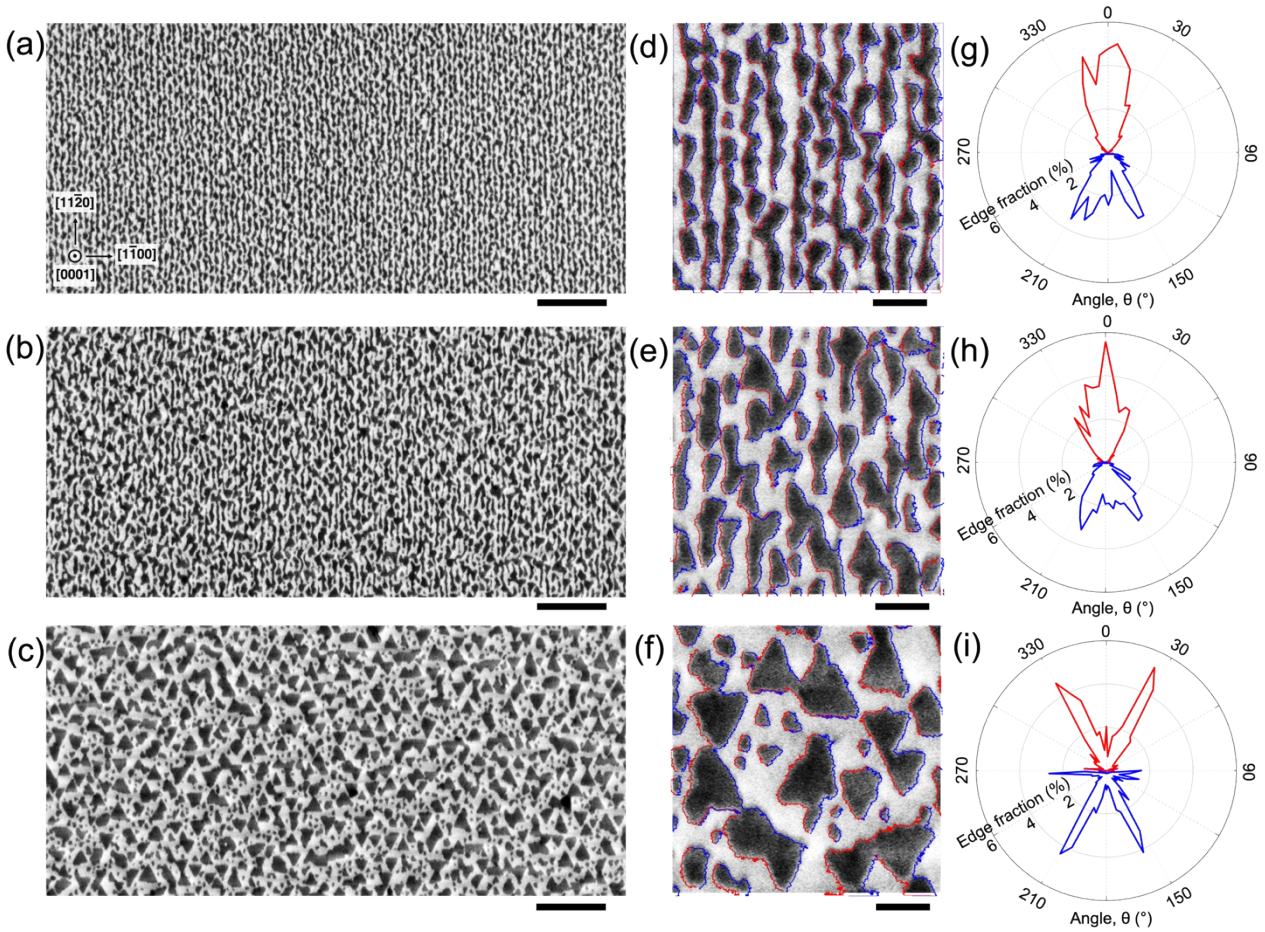

Figure S8. SEM images of $MoSe_2$ domains grown at 750 ℃ with (a) 0 → 10% H_2 (5 – 5 min), (b) 0 → 10% H_2 (5 – 10 min), and (c) 0 → 10% H_2 (5 – 15 min) conditions, showing the shift of domain alignment from along the substrate [11$\bar{2}$0] step-edges to rotated-alignment of triangular domains occurs in a broad range. Scale bars, 1 μm. (d – f) Magnified SEM images of (a – c) with the domain boundaries highlighted in colors; red corresponds to the left side and blue to the right side of the domain. Scale bars, 200 nm. (g – i) Polar plots of the $MoSe_2$ domain edge fractions measured from (d – f). The edge deviation angle, θ is as defined in main Figure 2. The left side (red) edge orientations are shown as distributed from 270° (or - 90°) to 90°, where the right side (blue) edge orientations from 90° to 270°. Although the individual domains observed in (d) and (e) appear to exhibit irregular edge orientations, the alignment observed from the left side (red) edges along the substrate [1120] orientation relative to (f) suggests that the step-edges are favorable sites for the initial nucleation. We measure a total of 1800 edge deviation angles from 600 $MoSe_2$ domains for each three conditions.

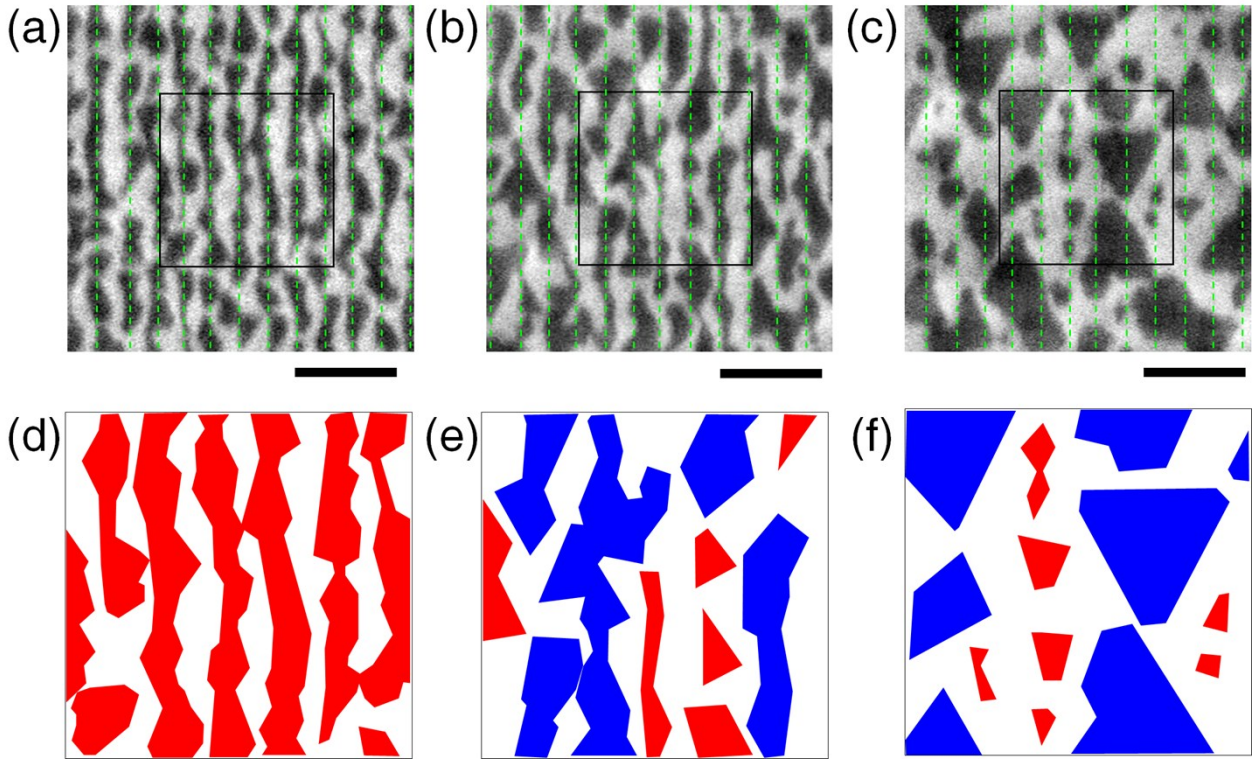

Figure S9. SEM images of $MoSe_2$ domains grown at 750 ℃ with (a) 0 → 10% H_2 (5 – 5 min), (b) 0 → 10% H_2 (5 – 10 min), and (c) 0 → 10% H_2 (5 – 15 min) conditions. Scale bar, 200 nm. The green dotted lines are drawn along the substrate [$11\bar{2}0$] orientation with the spacing of ~ 60 nm, which is similar to the average terrace width between surface steps. (d – f) Schematic drawings of $MoSe_2$ domains designated by black squares in (a – c). Domains whose width is thinner than the step width are colored in red, while those wider than the steps are in blue. Thin domains originally aligned along the substrate step edges decrease both in size and continuity, which suggests the etching effect by hydrogen.

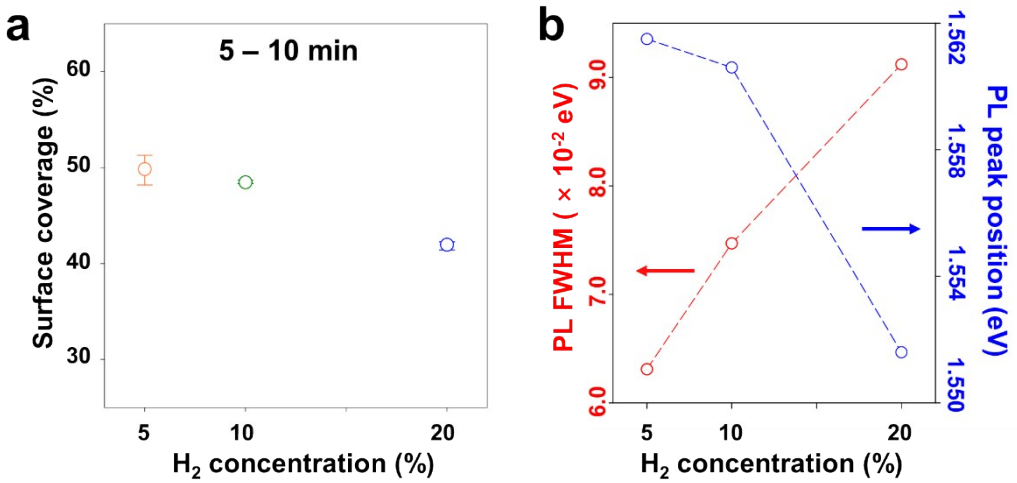

Figure S10. **(a)** Surface coverage of the $MoSe_2$ domains as a function of H_2 concentration at the same growth time (5 – 10 min). An average of 220 $MoSe_2$ was measured for each concentration. **(b)** Change in the full width at half-maximum (FWHM) and the peak position of photoluminescence (PL) spectra as a function of the H_2 concentration at a growth temperature of 750 ℃. Increasing FWHM and the red-shift of peaks indicate an increase in defect density and multilayer formation with increasing H_2 concentration.

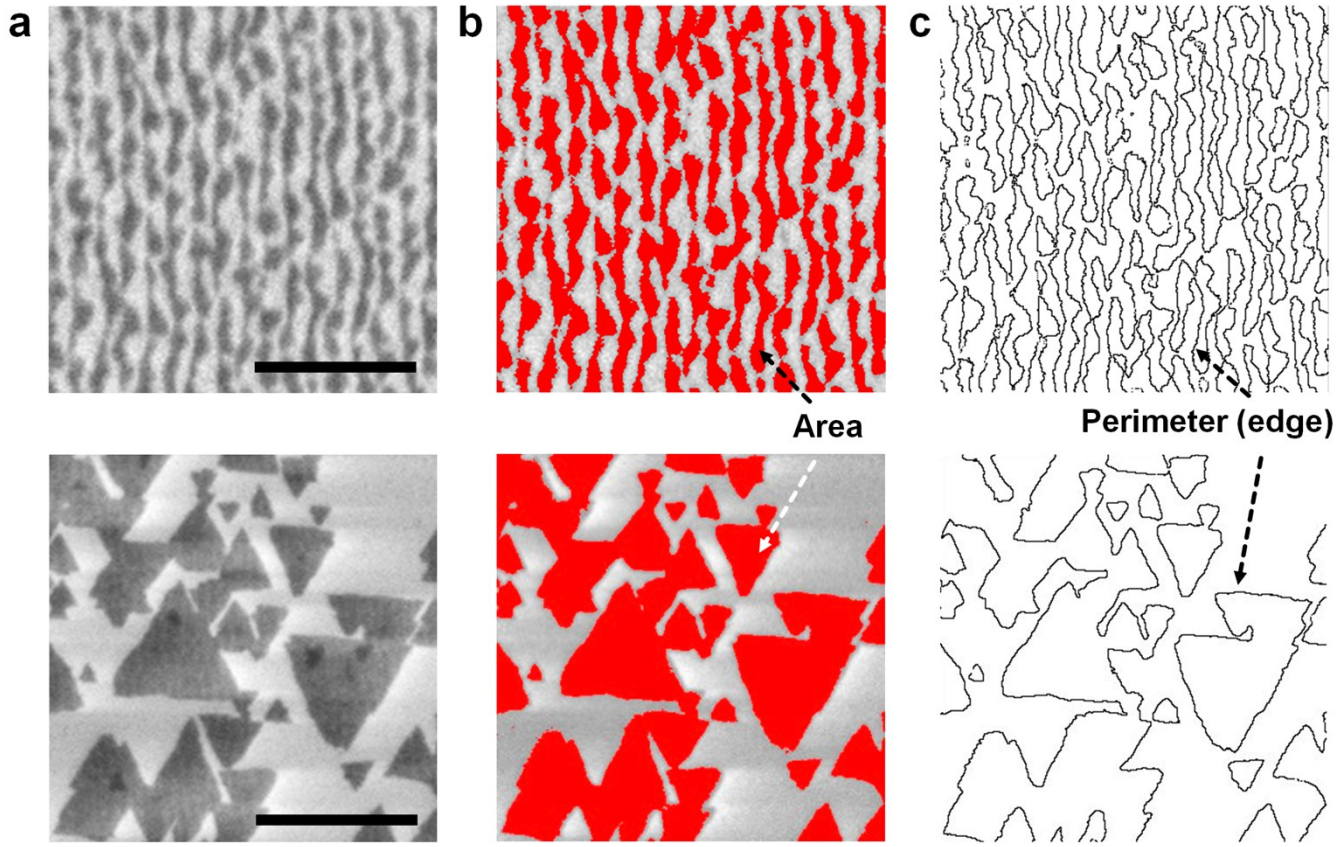

Figure S11. Surface coverage and the domain edge length to area ratio (E/A ratio) of $MoSe_2$ calculated using imageJ. **(a)** SEM images of representative $MoSe_2$ grown at 750 ℃ and 800 ℃, respectively. Scale bars, 400 nm (above) and 1 μm (below). **(b)** Using brightness thresholds function, $MoSe_2$ domains are marked by a red color. Domain area and the surface coverage are calculated. **(c)** Using "analyze particles" function, the perimeter of the red color highlighted region is calculated. The E/A ratio is obtained by dividing the total perimeter length in a designated region – three randomly chosen area with a size of 2 μm × 2 μm, by the corresponding total domain area in the region.