Electronic Supplementary Information (ESI)

Atomistic Dynamics of Sulfur-Deficient Grain Boundaries in Molybdenum Disulfide

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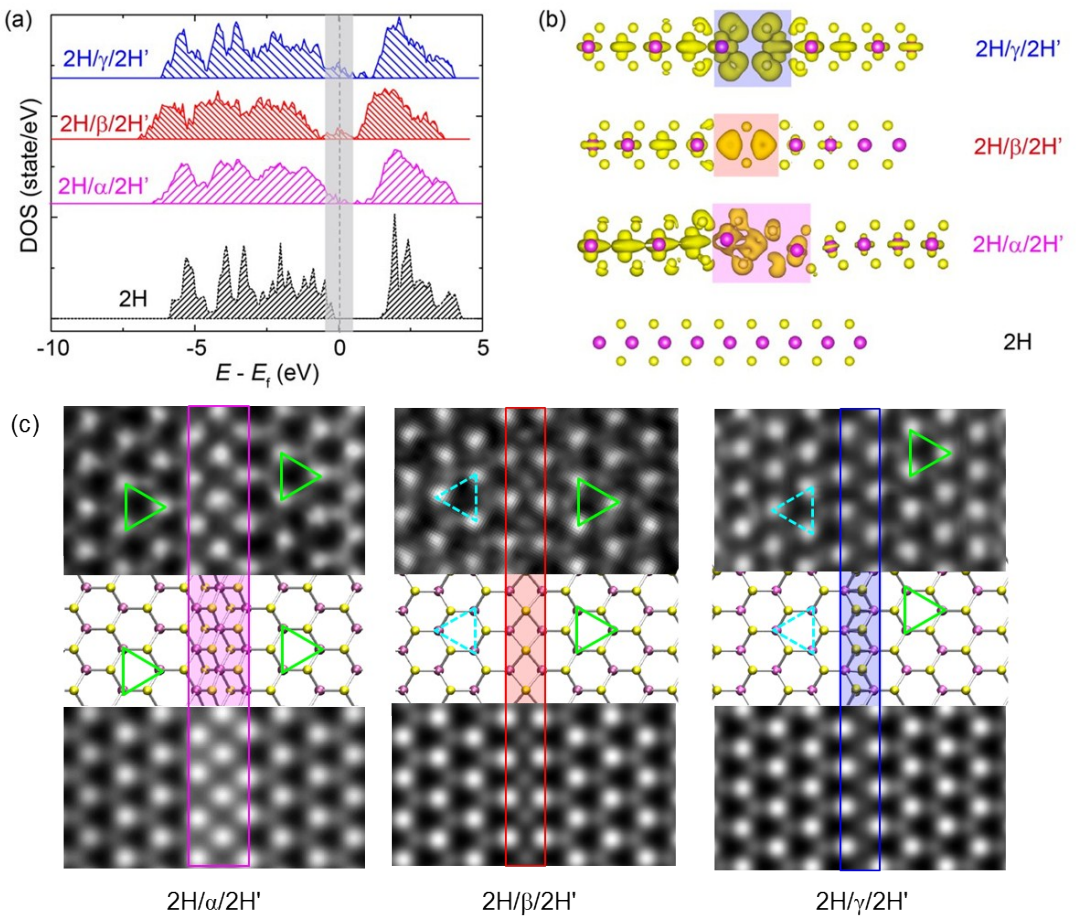

Figure S1. (a) Electronic DOS for the whole structure with GBs (α, β, γ-types) compared to that of crystalline 2H-MoS_2. (b) The partial charge densities of electronic states with energy within the range from E_F-0.5 eV to E_F+0.5 eV (gray windows in panel (a)), indicating that the electron states near the Fermi level are spatially localized near the GB. (c) A comparison of the experimental/simulated ADF images of α, β, γ-type GBs.

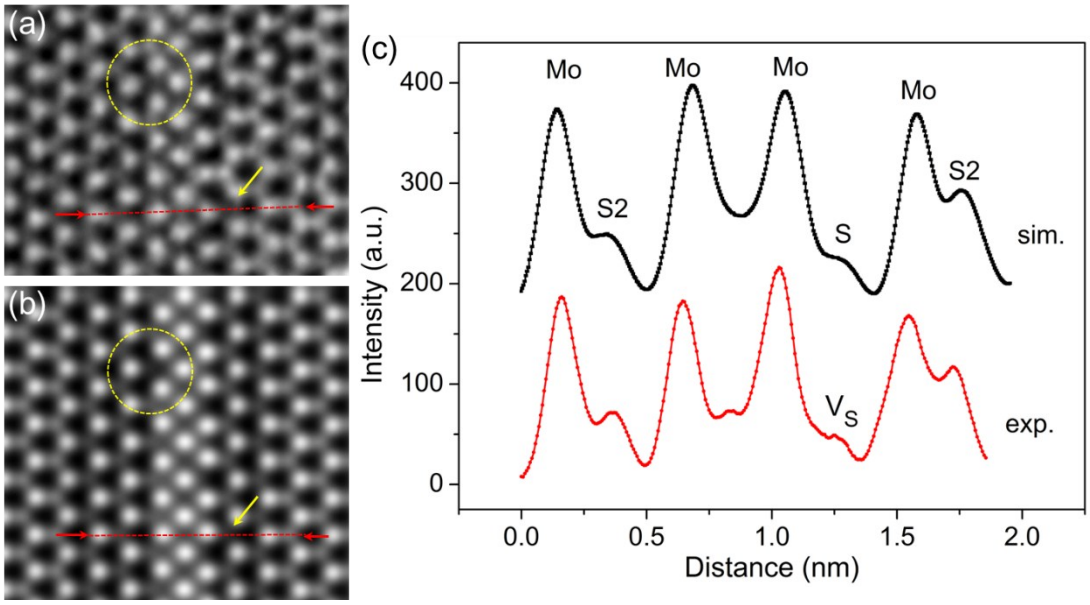

Figure S2. (a) Experimental ADF image of α-type GBs with vacancies nearby. (b) Simulated ADF image of α-type GBs. Yellow circles or arrows indicate S-vacancies. (c) ADF intensity line profiles along the red dashed lines in experimental/simulated images to confirm the existence of S vacancy.

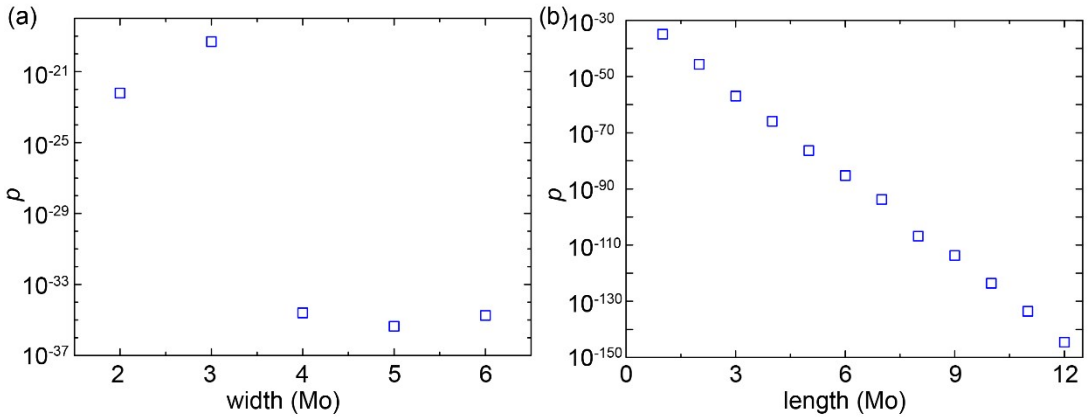

Figure S3. Probability of α-type GBs embedded in the 2H phase of MoS_2 with specific (a) width and (b) length, estimated by the Boltzmann factor $p_B = \exp(-E_f/k_BT)$ at T = 300 K. Here k_B = 8.617×10^{-5} eV/K is the Boltzmann constant.

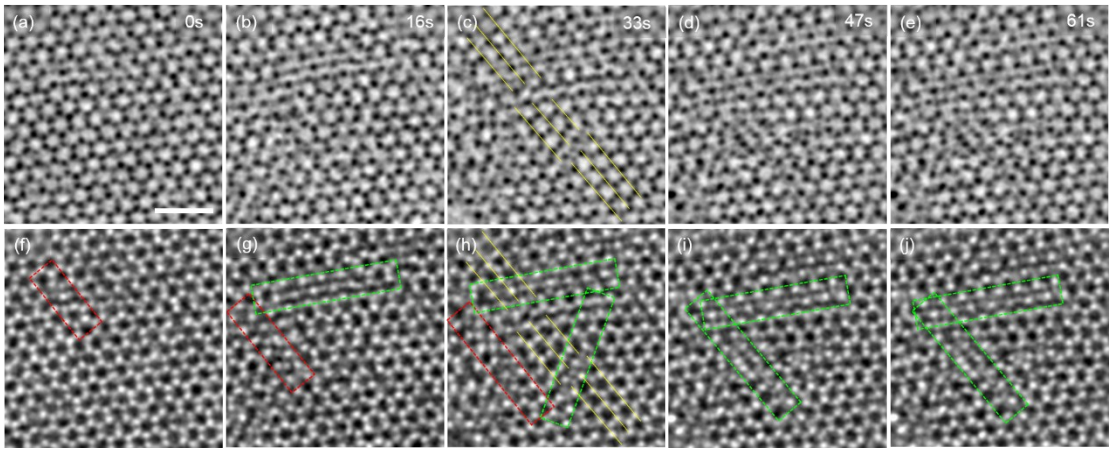

Figure S4. (a-e) Time sequential BF-STEM image series of monolayer MoS2 to show the formation and evolution of the inversion domains composed of β, γ -GBs. The partial dislocations are highlighted by yellow lines. Scale bar: 1 nm. (f-j) Contrast-inverted images corresponding to a-e, with β-GB highlighted in red rectangles and γ-GB in green.

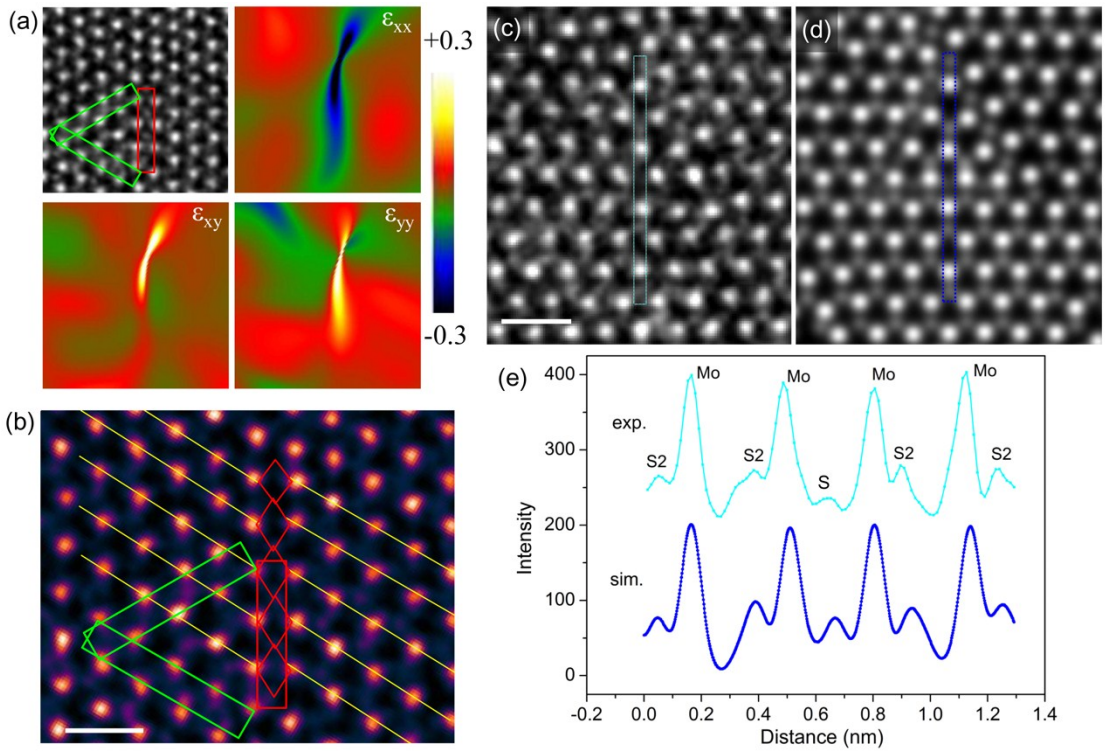

Figure S5. Strain distribution and structure analysis of GBs. (a) The inversion domain composed of *β*-type, *γ*-type GBs and its strain distribution revealed by the GPA analysis. (b) The partial dislocation properties of the inversion domain (**Fig. 4**) composed of *β*-type, *γ*-type GBs. Scale bar: 0.5 nm. (c,d) Experimental and simulated ADF images of the *γ*-type GBs in **Fig.4**. Scale bar: 0.5 nm. (e) Intensity line profiles along the long sides of stripes in c,d, where the single-S site and opposite orientation of Mo-S_2 pairs confirm the *γ*-type GBs.

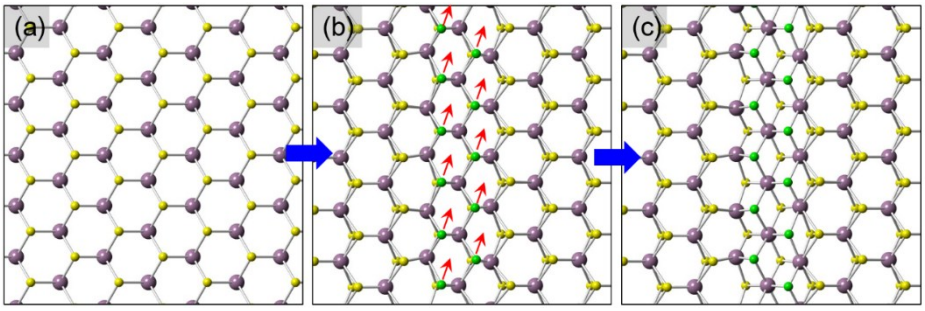

Figure S6. The formation mechanism of an α-type GB based on TEM-analyzed atomic structures. The migrating S atoms are highlighted by the arrows in the transition from 2H matrix to strained 1T α-type GB. Mo and S atoms are colored in purple and yellow, respectively. The slipping S atoms are highlighted in green color.

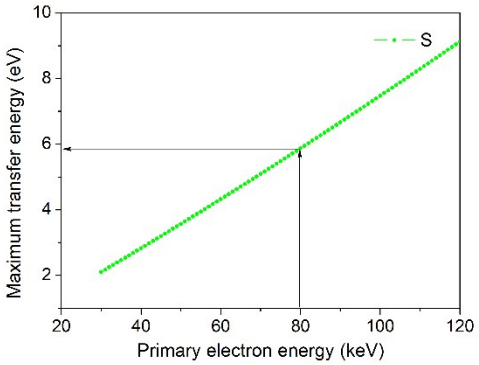

Figure S7. Beam-atom knock-on interaction. The maximum transfer energy is a function of primary energy or acceleration voltage. At 80 keV, the S-atoms could receive a kinetic energy up to 5.87 eV from the knock-on scattering of incident electrons.

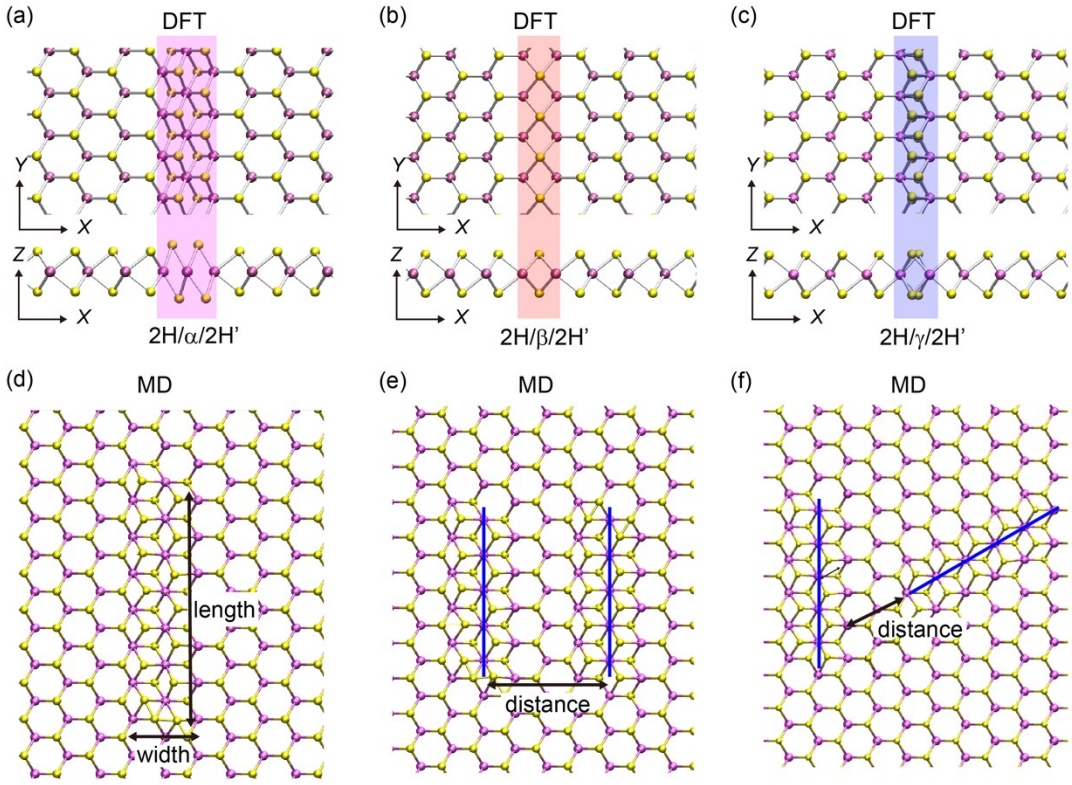

Figure S8. (a-c) Models for DFT calculations carried out to explore the formation energies of the three types of GBs, the effect of mono-vacancy on the formation energy of GB, and the energy barriers for a S-atom to migrate across a GB to the S-vacancy nearby for α-type and γ-type GBs. (d-f) Models for empirical potential based MD simulations performed to explore the effect of width and length on the formation energy for α-type GB, and the interactions between two α-type GBs.

Supplementary Notes

1. A kinetic model to predict the length distribution of *α*-type GBs

To analyze the length distribution of *α*-type GBs, we introduce a kinetic model as follows. From the results in **Fig. 3**, we find that the maximum length of GBs characterized in experiments is 12 Mo-units. We then assume that the length N of a finite-length GB is distributed in the range from 0 to 16, which can grow from a GB with N-1 or be degraded from a GB with N+1. The corresponding rates of reaction $k_+ = 0.41$, $k_- = 1 - k_+ = 0.59$ are determined from the energy barrier ΔE obtained from our DFT calculations, that is

$$k_+/k_- = \exp(2\Delta E/k_B T) \tag{S1}$$

Consequently, the population c_N of existing GBs with length N could be calculated from following equations:

$$c_0 = ak_0 + k_- c_1$$

$$c_N = k_+ c_{N-1} + k_- c_{N+1} \tag{S2}$$

$$\Sigma_N c_i = 1$$

Here ak_0 is the nucleation of a single Mo-unit, which can be neglected due to the much higher formation energy. On the other hand, the lifetime should also fit the Boltzmann factor due to the nature of thermal activation, that is

$$c_N = a\exp(-E_f/k_B T) \tag{S3}$$

Combing the scaling laws (Eqs. **S1** and **S2**), we find that the population of *α*-type GBs with length N is maximized at $N \sim 7$, which aligns with the experimental evidence (**Fig. 3d**).