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## Supplementary Information

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# Energetics and Kinetics of Phase Transition Between 2H and 1T $MoS_2$ Monolayer—a Theoretical Study

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## S1. Introduction The stability and the boundaries between 2H and 1T' phases

In equilibrium, an obvious initial concern is the structure and the lowest ground-state energy of the boundary, which readily yields the thermodynamically optimal shape using the Wulff construction. The stability of the boundaries is evaluated by their formation energy per unit length ($\gamma_b$), using the fitted value based on DFT calculations. $\gamma_b$ is calculated as follows.

(i) We denote $l$ as the length of the boundary and $\Delta m$ as the number of S atoms lost to ($\Delta m < 0$) or gained ($\Delta m > 0$) from the feedstock. So the formation energy $G_f$ of a triangular 1T phase inside the 2H monolayer is

$$G_f = E + \Delta m \times \mu_S - E_{2H} \quad \text{(S1)}$$

where $E$ and $E_{2H}$ are the DFT energies of the 2H monolayer with and without 1T phase inside, respectively, and $\mu_S$ is the chemical potential of the S feedstock.

(ii) $G_f$ can be viewed as contributed by three parts, i.e., the three vertices of the triangle ($\varepsilon_v$), the three boundaries ($\gamma_b$), and the 1T phase inside ($\delta$) whose area is $\sqrt{3}l^2/4$.

$$G_f = 3\varepsilon_v + 3l\gamma_b + \frac{\sqrt{3}}{4}l^2\delta \quad \text{(S2)}$$

(iii) For each kind of boundaries, we construct several (at least three) structures with different sizes (the number $n$ of honeycombs along one side, $l = l(n)$) and calculate their corresponding $E_f$, then we can fit those value and obtain $\gamma_b$ and $\delta$. In detail, we denote the lattice vector of $MoS_2$ monolayer (or the Mo-Mo distance) as $a$. For AC boundaries, we have $l = \sqrt{3}na - 2a/\sqrt{3}$, while for ZZ boundaries, $l = na$.

As the boundary length ($n$) increases, the number of S atoms ($\Delta m$) departed from stoichiometry also increases, following a linear relationship ($k_1$ and $k_2$ are parameters)

$$\Delta m = k_1 n + k_2 \quad \text{(S3)}$$

(iv) Combining the equations above, we can get ($A$, $B$, and $C$ are fitting parameters)

$$E - E_{2H} = An^2 + Bn + C \quad \text{(S4)}$$

For AC boundaries,

$$\begin{aligned} A &= \frac{3\sqrt{3}}{4}a^2\delta \\ B &= 3\sqrt{3}a\gamma_b - k_1\mu_S - \sqrt{3}a^2\delta \\ C &= 3\varepsilon_v - k_2\mu_S - 2\sqrt{3}a\delta + \frac{a^2\delta}{\sqrt{3}} \end{aligned} \quad \text{(S5a)}$$

For ZZ boundaries,

$$\begin{aligned} A &= \frac{\sqrt{3}}{4}a^2\delta \\ B &= 3a\gamma_b - k_1\mu_S \\ C &= 3\varepsilon_v - k_2\mu_S \end{aligned} \quad \text{(S5b)}$$

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(v) Then we can finally get the formation energy of the boundaries:

$$\gamma_b(AC) = \frac{B + k_1\mu_S + \sqrt{3}a^2\delta}{3\sqrt{3}a} \quad \text{(S6a)}$$

$$\gamma_b(ZZ) = \frac{B + k_1\mu_S}{3a} \quad \text{(S6b)}$$

## S2. Nucleation of 1T phase inside 2H phase

**Table S1**. The parameters fitted from DFT energies ($A$, $B$, and $C$) and structures ($k_1$, $k_2$, $A'$, $B'$, and $C'$). $\delta$ is in the unit of eV/Å$^2$. $\Delta\mu_c$ is in the unit of eV/$MoS_2$.

| | $E - E_{2H} = An^2 + Bn + C$ | | | $\delta$ | $\Delta m = k_1 n + k_2$ | | $N_{1T} = A'n^2 + B'n + C'$ | | | $\Delta\mu_c$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | $A$ | $B$ | $C$ | | $k_1$ | $k_2$ | $A'$ | $B'$ | $C'$ | |
| **ZZ-Mo\|-** | 0.287 | 5.731 | 1.911 | 0.065 | 1 | 0 | 0.5 | -0.5 | 0 | 0.573 |
| **ZZ-Mo\|+** | 0.195 | -4.524 | 29.405 | 0.044 | -2 | 12 | 0.5 | -0.5 | -9 | 0.390 |
| **ZZ-S\|-** | 0.237 | 13.771 | -21.793 | 0.054 | 2 | -3 | 0.5 | -0.5 | -9 | 0.474 |
| **ZZ-S\|+** | 0.226 | -1.401 | 14.678 | 0.051 | -1 | 7 | 0.5 | -0.5 | -9 | 0.452 |
| **AC\|-** | 0.758 | 18.820 | -5.006 | 0.057 | 3 | -1 | 1.5 | -1.5 | 1 | 0.505 |
| **AC\|+** | 0.842 | 5.692 | 7.549 | 0.063 | 0 | 2 | 1.5 | 1.5 | -2 | 0.561 |

The change in Gibbs free energy $G_f$ as a function of the nucleus size $n$ or $N_{1T}$ dominates the behavior of nucleation. Then from $G_f$ in Eq. (3) in the main text, we can furthermore analyze how a 1T phase nucleates inside a 2H lattice. Now we focus on the nuclei with ZZ-Mo|- and ZZ-S|+ boundaries, which has lower formation energy and then higher chance to present. Since the number of S atoms hoped to 1T phase ($N_{1T}$) has a polynomial relationship with $n$ ($N_{1T} = A'n^2 + B'n + C'$, all the coefficients listed in Table S1.), we can rewrite $G_f$ in Eq. (3) and (S4) as

$$G_f = (A - A'\Delta\mu)n^2 + (B - B'\Delta\mu + k_1\mu_S)n + (C - C'\Delta\mu + k_2\mu_S) \quad \text{(S7)}$$

and $N_{1T}$ is the number of the top-layer S atoms in the 1T phase which is proportional to the area of the 1T phase in the 2H lattice and represents the size of the 1T phase. $\Delta\mu$ is the chemical potential difference between 1T and 2H phases.

In eq.(3), $G_f = E + \Delta m \times \mu_S - E_{2H} - N_{1T}\Delta\mu$, the term $-N_{1T}\Delta\mu$, represents the formation energy drop of the nucleated 1T' phase as a result of doping or charge transfer. It will affect the stability of different boundaries accordingly:

$$\gamma_b(AC) = \frac{B - B'\Delta\mu + k_1\mu_S + \sqrt{3}a^2\delta}{3\sqrt{3}a} \quad \text{(S8a)}$$

$$\gamma_b(ZZ) = \frac{B - B'\Delta\mu + k_1\mu_S}{3a} \quad \text{(S8b)}$$

Note that the parameter $B'$ is the same for ZZ boundaries as shown in Table S1, therefore, the driving force $\Delta\mu$ will not affect the relative stability between ZZ boundaries.

The nucleus size and nucleation barrier ($n^*$, $G^*$), are defined as the maximum of the $G_f(n)$ curve at a given $\Delta\mu$ and $\mu_S$. Following this definition, we can easily determine $G^*$ and $n^*$ as a function of $\Delta\mu$ at a given $\mu_S$, through $\left.\frac{\partial G}{\partial n}\right|_{n=n^*} = 0$, and $\left.\frac{\partial^2 G}{\partial n^2}\right|_{n=n^*} < 0$.

$$n^* = \frac{B - B'\Delta\mu + k_1\mu_S}{2(A'\Delta\mu - A)}, \Delta\mu > \Delta\mu_c = \frac{A}{A'}$$
$$G^* = \frac{(B - B'\Delta\mu + k_1\mu_S)^2}{4(A'\Delta\mu - A)} + (C - C'\Delta\mu + k_2\mu_S) \quad \text{(S9)}$$

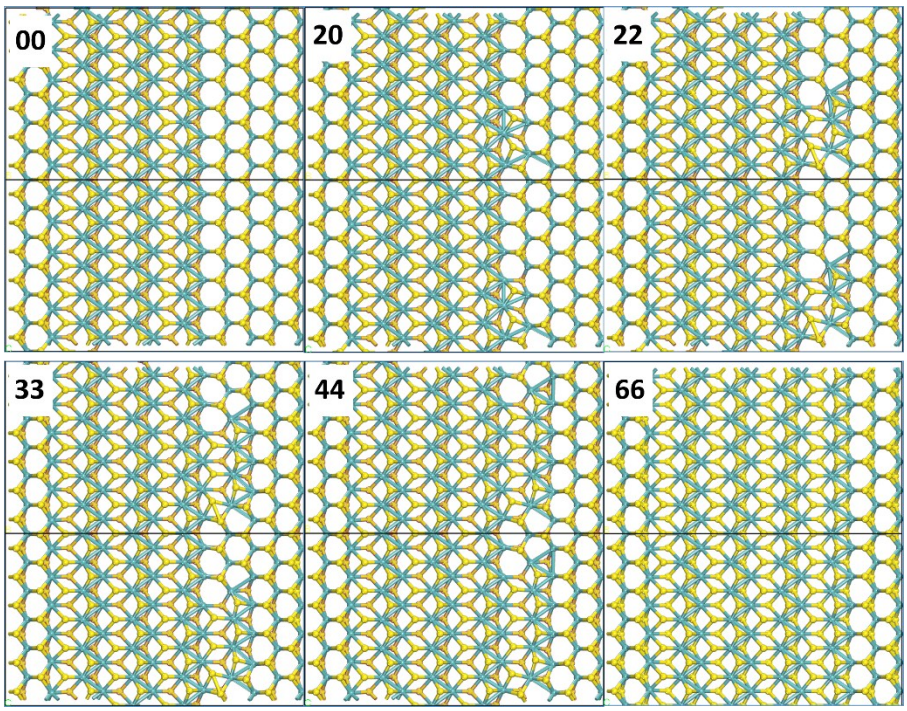


**Figure S1.** The step-flow model at the ZZ-Mo|- boundary. The migrated S atoms in both rows $(i,j) = (0,0)$, $(2,0)$, $(2,2)$, $(3,3)$, $(4,4)$ and $(6,6)$ respectively. 2×2 supercells are used in all figures to show the structures clearly.

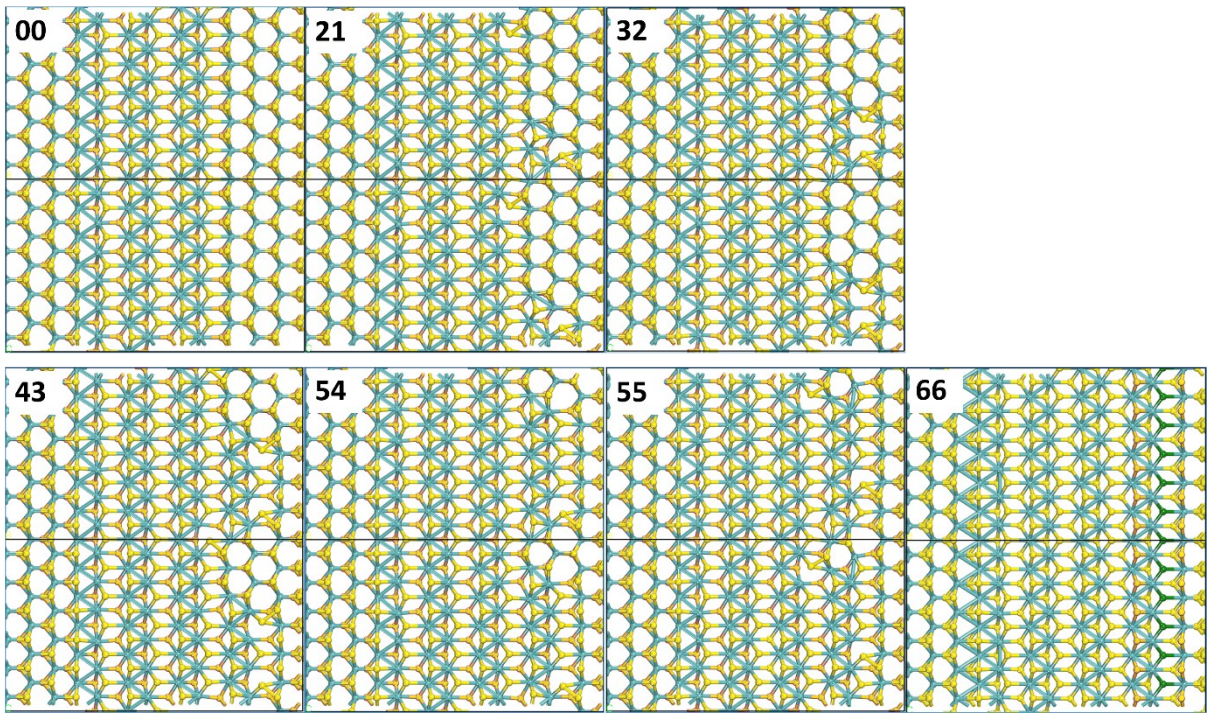


**Figure S2**. The step-flow model at the ZZ-Mo|+ boundary. The migrated S atoms in both rows $(i,j) = (0,0)$, $(2,1)$, $(3,2)$, $(4,3)$, $(5,4)$, $(5,5)$ and $(6,6)$, respectively.

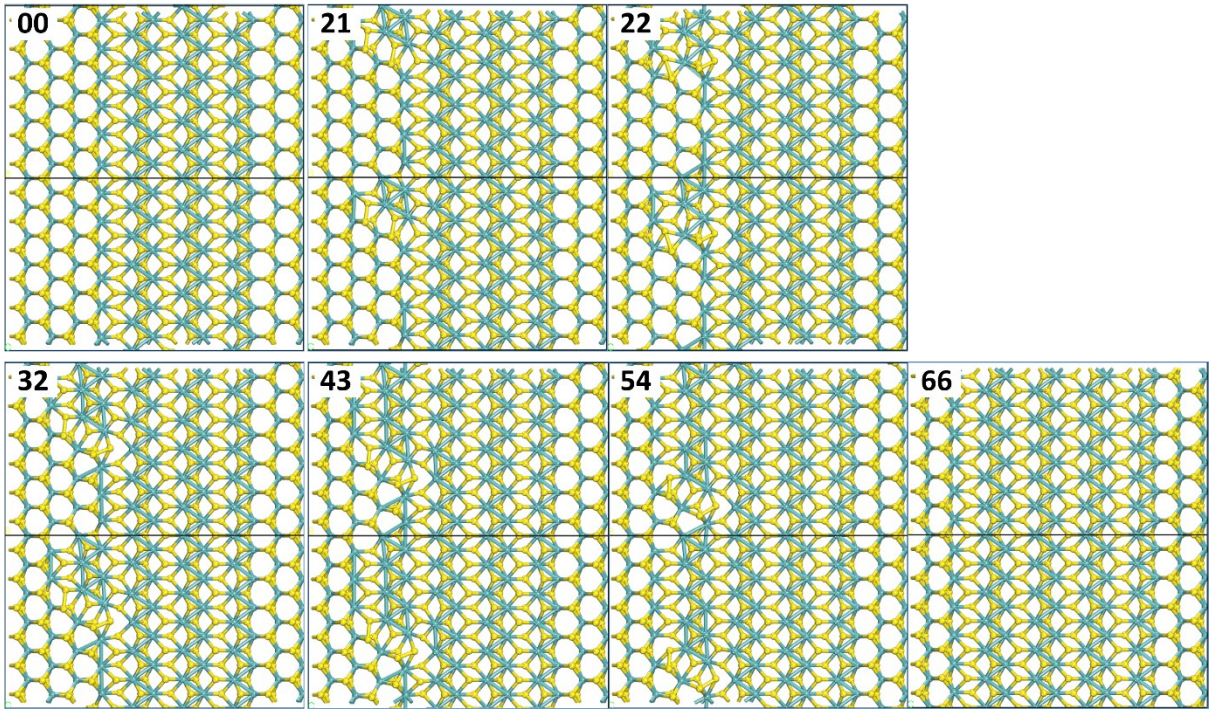


**Figure S3**. The step-flow model at the ZZ-S|+ boundary. The migrated S atoms in both rows $(i,j) = (0,0)$, $(2,1)$, $(2,2)$, $(3,2)$, $(4,3)$, $(5,4)$ and $(6,6)$ respectively.