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Initial stage of atomic layer deposition of 2D-MoS$_2$ on SiO$_2$ surface: a DFT study

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Supporting information (SI) contains two figures and two tables.

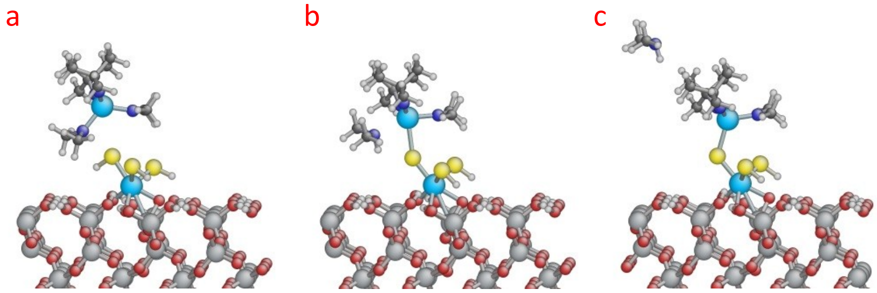

Figure S1. Introduction of $Mo(NMe_2)_2(N^tBu)_2$ precursor to the formed SH groups at the fully hydroxylated SiO_2 (0001) surface. These reactive sites are formed in previous cycles of ALD which perform as nucleation sites in the metal pulse of ALD. Here, only reaction energies of formation and desorption of dimethylamine are calculated which shows that the course of chemical reactions are the same as the fully hydroxylated SiO_2 surface. (a) Shows the initial configuration of physisorbed precursor $Mo(NMe_2)_2(N^tBu)_2$. The Lewis basicity of the terminal SH and Lewis acidity of MoX_2Y_2 is not strong enough to gives rise to chemical adsorption of precursor which is similar to the equivalent introduction of $Mo(NMe_2)_2(N^tBu)_2$ to the terminal OH group at the fully hydroxylated SiO_2 (0001) surface (b) Shows the protonated precursor. Proton transfer to dimethylamido ligands gives rise to chemical adsorption of the physisorbed precursor. The picture of chemical adsorption of $Mo(NMe_2)_2(NtBu)_2$ on the terminal SH group at the SiO_2 surface is the same as adsorption of $Mo(NMe_2)_2(N^tBu)_2$ on the terminal OH group at the SiO_2 surface. The described picture is in contrast to the common knowledge of chemical adsorption of metal precursors and subsequent protonation of ligands. The bond length between Mo and N is increased from 2.06 Å to 2.46 Å. This reaction is exothermic by 1.13 eV. (c) Desorption of first dimethylamine as protonated ligand. This reaction is endothermic by 0.22 eV.

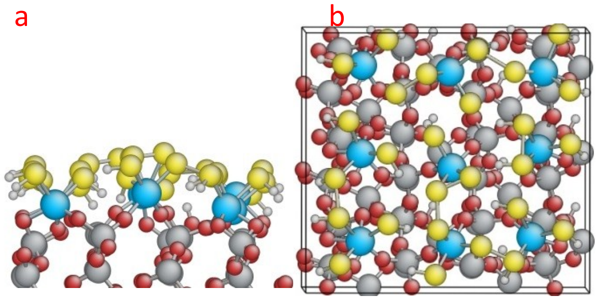

Figure S2. Formation of the buffer-layer at the interface by the cyclical reactions of ALD. (a) Shows the side view of the formed layer at the top of fully hydroxylated SiO_2 (0001) surface. Mo atoms covalently bond to 3 O at the SiO_2 surface and 3 S at the top layer, while S atoms covalently bond to Mo or neighboring S. Hence, Mo has coordination number (c.n.) of 6 while S has either 1 c.n. or 2 c.n. (excluding H). (b) Shows the top view of the formed layer. 9 Mo and accordingly 27 S are being optimized at the SiO_2 (0001) surface. These numbers are considered according to the course of ALD reactions which terminated to 6 coordinated Mo at the interface. Considering higher number of Mo in the surface area leads to the formation of low coordinated Mo at the interface. Such morphology at the interface is not fully optimized and does not follow the course of ALD reactions.

Table 1. Adsorption energies of MoX_2Y_2 and activation energy of proton transfer for different OH-coverages, the vdW functionals (opt) is included here. The 'optPBE-vdW' has been chosen to treat the reaction energy of ALD reactions. The inclusion of vdW interaction makes the adsorption more favorable.

Reaction	OH-coverage	ΔE (eV)	$\Delta G^{500K}(\Delta G^{298K})$ (eV)	Reactive site involved in reaction
1. $MoX_2Y_2(g) \rightarrow MoX_2Y_2{}^*$	2 ML O and 2 ML H	-0.72	+1.01 (+0.25)	Terminal OH
2. $MoX_2Y_2(g) \rightarrow MoX_2Y_2{}^*$	1.75 ML O and 1.50 ML H	-1.03	+0.70 (-0.05)	Terminal OH
3. $MoX_2Y_2(g) + 2OH(s) \rightarrow MoH_2X_2Y_2(s) + 2O(s)$	1.75 ML O and 1.50 ML H	-4.45	-1.72(-3.46)	Terminal O
4. $MoX_2Y_2{}^* + OH(s) \rightarrow MoHX_2Y_2(s) + O(s)$	2 ML O and 2 ML H	+0.15	+1.89 (+1.14)	Terminal OH
5. $MoHX_2Y_2(s) + OH(s) \rightarrow MoH_2X_2Y_2(s) + O(s)$	2 ML O and 2 ML H	-0.12	---	Terminal OH
6. $MoX_2Y_2{}^* + OH(s) \rightarrow MoHX_2Y_2{}^* + O(s)$	1.75 ML O and 1.50 ML H	-0.01	+1.72 (+0.96)	Terminal OH
7. $MoHX_2Y_2{}^* \rightarrow MoHX_2Y_2(s)$	1.75 ML O and 1.50 ML H	-0.60	+1.13 (+0.38)	Terminal O
8. $MoHX_2Y_2(s) + OH(s) \rightarrow MoH_2X_2Y_2(s) + O(s)$	1.75 ML O and 1.50 ML H	-0.17	---	Terminal OH
9. $MoXY_2(s) + OH(s) \rightarrow MoHXY_2(s) + O(s)$	2 ML O and 2 ML H	-0.08	---	Terminal OH
10. $MoY_2(s) + OH(s) \rightarrow MoHY_2 + O(s)$	2 ML O and 2 ML H	-0.23	---	Terminal OH
11. $MoY_2(s) + OH(s) \rightarrow MoHY_2 + O(s)$	1.75 ML O and 1.50 ML H	-1.79	---	Bridging OH
12. $MoY_2(s) + OH(s) \rightarrow MoHY_2 + O(s)$	1.75 ML O and 1.50 ML H	+0.45	---	Terminal OH
13. $O(s) + OH(s) \rightarrow OH(s) + O(s)$	1.75 ML O and 1.50 ML H	-2.16	---	Bridging OH

* Shows the physisorbed precursor. Gibbs free energy ΔG are given in two different temperatures T = 500 K and T = 298.15 K (in parenthesis).

Table 2. Activation energy and reaction energy of H_2S adsorption, H_2S dissociation, and desorption of protonated ligands. The inclusion of vdW interaction makes the adsorption more favorable and the desorption more unfavorable.

Reaction	OH-coverage	ΔE (eV)	$\Delta G^{500K}(\Delta G^{298K})$ (eV)	Initial c.n. of Mo
1. $MoH_2X_2Y_2(s) \rightarrow MoHXY_2(s) + HX(g)$	2 ML O and 2 ML H	+0.06	-1.30 (-0.70)	c.n.=5
2. $MoHXY_2(s) \rightarrow MoY_2(s) + HX(g)$	2 ML O and 2 ML H	+0.93	-0.43 (+0.17)	c.n.=4
3. $MoH_2X_2Y_2(s) \rightarrow MoHXY_2(s) + HX(g)$	1.75 ML O and 1.50 ML H	+0.67	-0.69 (-0.09)	c.n.=5
4. $MoHXY_2(s) \rightarrow MoY_2(s) + HX(g)$	1.75 ML O and 1.50 ML H	+1.19	-0.16 (+0.43)	c.n.=4
5. $MoHY_2(s) + H_2S(g) \rightarrow MoHY_2(s) + H_2S(s)$	2 ML O and 2 ML H	-0.55	+0.59 (+0.07)	c.n.=5
6. $MoHY_2(s) + H_2S(g) \rightarrow MoH_2Y_2(s) + SH(s)$	2 ML O and 2 ML H	-0.50	+0.63 (+0.12)	c.n.=5
7. $MoY_2(s) + H_2S(g) \rightarrow MoY_2(s) + H_2S(s)$	1.75 ML O and 1.50 ML H	-0.40	+0.73 (+0.22)	c.n.=4
8. $MoHY_2(s) + H_2S(g) \rightarrow MoHY_2(s) + H_2S(s)$	1.75 ML O and 1.50 ML H	-0.04	+1.10 (+0.59)	c.n.=4
9. $MoY_2(s) + H_2S(g) \rightarrow MoHY_2(s) + SH(s)$	1.75 ML O and 1.50 ML H	-0.33	+0.81 (+0.29)	c.n.=4
10. $MoH_3Y_2(s) \rightarrow MoHY(s) + H_2Y(g)$	2 ML O and 2 ML H	+0.49	-0.97 (-0.33)	c.n.=6
11. $MoHY(s) + H_2S(g) \rightarrow MoH_2Y(s) + H_2S^*$	2 ML O and 2 ML H	-0.30	+0.84 (+0.32)	c.n.=5
12. $MoHY(s) + H_2S(g) \rightarrow MoH_2Y(s) + SH(s)$	2 ML O and 2 ML H	+0.15	+1.30 (+0.78)	c.n.=5
13. $MoH_2Y(s) \rightarrow Mo(s) + H2Y(g)$	2 ML O and 2 ML H	+0.97	-0.49 (+0.15)	c.n.=6
14. $MoH_2Y(s) + H_2S(g) \rightarrow MoH_2Y(s) + H_2S(s)$	2 ML O and 2 ML H	-0.02	+1.12 (+0.60)	c.n.=6
15. $MoH2Y(s) \rightarrow Mo(s) + H2Y(g)$	2 ML O and 2 ML H	-0.80	-2.27 (-1.63)	c.n.=7
16. $H_2S^* + OH(s) \rightarrow SH(s) + OH(s)$	2 ML O and 2 ML H	-0.90	---	---

* Shows the physisorbed precursor. Gibbs free energy ΔG are given in two different temperatures T = 500 K and T = 298.15 K (in parenthesis).