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Citation for published version (APA):

Shirazi, M., Kessels, W. M. M., & Bol, A. A. (2018). Initial stage of atomic layer deposition of 2D-MoS₂ on a SiO₂ surface: A DFT study. *Physical Chemistry Chemical Physics*, 20(24), 16861-16875.
<https://doi.org/10.1039/c8cp00210j>

DOI:

[10.1039/c8cp00210j](https://doi.org/10.1039/c8cp00210j)

Document status and date:

Published: 28/06/2018

Document Version:

Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Initial stage of atomic layer deposition of 2D-MoS₂ on SiO₂ surface: a DFT study

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KEYWORDS: DFT, 2D materials, ALD.

ABSTRACT: In this study, we investigate the reactions involving Atomic Layer Deposition (ALD) of 2D-MoS₂ from the heteroleptic precursor Mo(NMe₂)₂(N^tBu)₂ and H₂S as co-reagent on the SiO₂(0001) surface by means of density functional theory (DFT). All dominant reaction pathways from early stage of adsorption of each ALD reagent to the formation of bulk-like Mo and S at the surface are identified. In the metal pulse, proton transfer from terminal OH groups on the SiO₂ to the physisorbed metal precursor increases the Lewis acidity of Mo and Lewis basicity of O, which gives rise to the chemical adsorption of metal precursor. Proton transfer from the surface to the dimethylamido ligands leads to the formation and desorption of dimethylamine. In contrast, the formation and desorption of tert-butylamine is not energetically favorable. The tert-butylimido ligand can only be partially protonated in the metal pulse. In the sulphur pulse, co-adsorption and dissociation of H₂S molecules gives rise to the formation and desorption of tert-butylamine. Through the calculated activation energies, the cooperation between H₂S molecules ('cooperative' mechanism) is shown to have a profound influence on the formation and desorption of tert-butylamine, which are crucial steps in the initial ALD deposition of 2D-MoS₂ on SiO₂. The cyclical ALD reactions gives rise to the formation of a buffer layer which might have important consequences for the electrical and optical properties on the 2D layer formed in the subsequent homodeposition.

Introduction.

The discovery of two-dimensional (2D) transition metal dichalcogenides (TMDs) has attracted great interest from the fields of electronics¹, optoelectronics², and catalysis³⁻⁴. This is mainly due to their unique and tunable electronic properties⁵. In parallel with the advances in above fields, the growth of high-quality thin-films with targeted functionality has incited an incredible amount of work.

TMDs, like graphene, have traditionally been isolated via top-down methods like mechanical exfoliation⁶, solution sonication⁷, and electrochemical exfoliation⁸. These methods show low yield, small lateral dimensions, or poor quality. A number of vapor-phase techniques like metal thin-film sulfurization⁹, metal oxide thin-film sulfurization¹⁰, and chemical vapor deposition¹¹⁻¹² have therefore been investigated to grow mono- to a few-layers of TMDs at the wafer-scale. In these methods, high temperatures (>500 °C) are typically utilized to deposit the thin-film. These high temperatures are often not compatible with the fabrication of electronic devices. Hence, one of the biggest challenges is the large-scale growth of free standing mono- or few-layers of TMDs at low temperatures to enable the scalable fabrication of atomically 2D thin-film for high performance devices.

Atomic layer deposition (ALD) is a deposition technique that consists of cyclic surface reactions of subsequent exposure of a precursor and a co-reagent to the surface. Owing to its self-limiting chemistry, ALD offers unique possibilities for high-quality, low temperature growth¹³⁻¹⁴ (<450 °C) of conformal thin-films with Å level thickness control. A first successful demonstration of a low temperature process flow for integration of back-gated 2D transistors in the BEOL (Back End Of Line), which included ALD of 2D-WS₂, has been reported recently¹⁵. Hence, ALD seems amenable to deposit 2D thin-film directly on the substrate. Although promising, so far only a limited number of experimental papers have appeared on ALD of 2D TMDs. Most studies concentrate on MoCl₅ and Mo(CO)₆ precursor¹⁶⁻¹⁷ with H₂S or CH₃SSCH₃ as the co-reagent. Lately also a study appeared in which Mo(NMe₂)₄ was used as the ALD precursor¹⁴.

For growth of thin-films by ALD, precursors need to be designed in such a way that the precursors are highly reactive toward the surface. Similarly the co-reagent, such as H₂O, H₂S, or H₂, should be highly reactive toward the deposited surface with remaining precursors. The precursor also must be volatile, thermally stable at growth temperature, ideally the reaction byproducts should be nonreactive and noncorrosive, and the reaction byproducts ultimately should not be incorporated into the thin-film. As required, design of ALD precursor chemistry has therefore proceeded from halides, alkoxides, β-diketonates, and alkyls compounds to dialkylamido/alkylimido compounds¹⁸. These dialkylamido precursors easily react with the growing thin-film through a multiple proton transfer pathway¹⁹, allowing deposition of thin films at relatively low temperatures. The by-products are protonated ligands which are chemically inert by their strong C-H and N-H bonds, and are therefore non-reactive and non-corrosive unlike the byproducts of halide and carbon-monoxide precursors.

The most extensively studied homoleptic (all ligands identical) amido metal precursors are those with dialkylamido groups²⁰⁻²². Homoleptic dialkylamido metal precursors with oxidation states of 4 or more are the most volatile. However, metal precursors with oxidation states higher than 4 do not show good thermal stability at high growth temperature¹⁴. Therefore, heteroleptic (not all ligands identical) compounds with mixed dialkylamido/alkylimido compounds have been synthesized for ALD. Heteroleptic compounds like $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ have successfully been used for the ALD of nitride²³⁻²⁴ and oxide²⁵⁻²⁶ thin-films. Therefore, in this study we concentrate on the ALD of MoS_2 from $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2/\text{H}_2\text{S}$ on the $\text{SiO}_2(0001)$ surface.

So far, theoretical work on the dominant reaction pathways of ALD chemistry have dealt with homoleptic metal precursors, like growth of HfO_2 from $\text{Hf}(\text{NMe}_2)_4/\text{H}_2\text{O}$, in steady state deposition²⁷. Essentially the identified reaction pathways in steady state deposition are then utilized as chemical identifier to investigate the success or failure of ALD deposition. The heteroleptic compound $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ is less symmetrical than $\text{Hf}(\text{NMe}_2)_4$ and the alkylimido ligand needs two proton transfers to form tert-butylamine²⁸.

Deposition of MoS_2 is initiated by the exposure of metal precursor $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ to the SiO_2 surface and then followed by the exposure of H_2S as co-reagent in second pulse. The initial nucleation at the substrate depends on the coverage of functional groups, partial pressure of precursors, and reactor conditions. In this so-called heterodeposition, functional groups are mainly OH and O groups at the surface. Different coverage of functional groups gives rise to different chemical reactivity at the surface. Hence, the chemical reactivity of precursors to the different coverage of functional group and reactor conditions determine the nucleation of 2D thin-films.

In this contribution, we will investigate the course of ALD reactions according to the coverage of reactive groups on the surface. Here, chemically reactive sites are those ones which contribute to the ALD reactions. Two different surfaces have been considered. First, a fully hydroxylated coverage is considered and in the second case, $3\text{H}_2\text{O}$ molecules have been removed from the surface. In the former case, only terminal OH-groups are reactive on the $\text{SiO}_2(0001)$ surface, while in the latter case, different reactive sites are formed at the reduced surface of $\text{SiO}_2(0001)$, due to the removal of H_2O molecules. The dominant reaction pathways of ALD deposition of 2D MoS_2 from the exposure of $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2/\text{H}_2\text{S}$ precursor on the two $\text{SiO}_2(0001)$ surfaces are identified. We will show how the initial situation of the surface and increase of pressure and temperature could potentially shorten the incubation period.

The cyclical ALD reactions terminate in the formation of highly coordinated Mo and S at the SiO_2 surface which ultimately gives rise to the formation of a buffer-layer. In such morphology, Mo atoms in the buffer-layer share the chemical bonds with O at the SiO_2 surface and S at the top layer. The formation of such a buffer-layer can have an essential influence on the electrical and the optical properties of a device, as was the case for epitaxial growth of graphene on SiC ²⁹⁻³¹. Similar behavior is expected for ALD growth of MoS_2 on a SiO_2 surface.

After formation of the buffer layer, ALD growth will enter into the steady-state deposition, called homodeposition. In homodeposition, SH and S group are the main functional groups which determine the chemical reactivity of the surface to the incoming precursors. In this contribution we concentrate on the heterodeposition, while the ALD reactions of homodeposition of MoS_2 will be reported in future work.

Computational details

To study the deposition of MoS_2 thin-film on the $\text{SiO}_2(0001)$ surface, self-consistent DFT calculations in the GGA approximation are employed. Reaction energies, activation energies and ab initio molecular dynamics of the system are calculated in a 3D periodic model, using VASP³². In these calculations, the electronic energies are approximated using the projector augmented wave (PAW)³³ description of atomic cores and the functional of Perdew, Burke, and Ernzerhof (PBE)³⁴. The plane wave cutoff energy is set to 600 eV. For Mo atoms $4d^55s^1$, S atoms $3s^23p^4$, N atoms $2s^22p^3$, C atoms $2s^22p^2$, O atoms $2s^22p^4$, and Si atoms $3s^23p^2$ electrons are included as valence electrons. The self-consistent steps are converged to an energy difference of at least 10^{-4} eV. Geometries are optimized using the conjugate-gradient scheme without symmetry restraints or fixed atoms, to a convergence of energy gradients of less than 10^{-3} eV/Å. Since the magnetic properties are essential for an accurate description of the energetics and kinetics³⁵, all calculations are spin-polarized.

The self-consistent electron density is performed by iterative diagonalization of the Kohn-Sham Hamiltonian, and all total energies are calculated at zero temperature. Since crystalline atoms are usually tightly packed and the typical temperature of interest is relatively low (comparing with the melting temperature), the harmonic approximation to transition state theory (hTST) can typically be used in studies of reactions at the crystalline surface³⁶⁻³⁷.

Converged values of the surface energies of the $\text{SiO}_2(0001)$ surface shows that five layers of SiO_2 are enough to be considered as a slab. To avoid slab-slab interaction in the periodic model, a vacuum region of 20 Å above the surface is imposed. The k-point sampling in reciprocal space is generated by the Monkhorst-Pack method. $8 \times 8 \times 8$ and $4 \times 4 \times 2$ grid sizes are utilized for bulk and slab, respectively. For the surface, we use a five-layered 3×3 supercell and the k-point sampling is reduced to $2 \times 2 \times 1$. Each layer of the slab has 12 Si atoms and is considered as a mono-layer (ML). The coverage of OH-atoms is calculated based on the number of OH-atoms divided by the number of Si atoms in a ML. Hence, the fully hydroxylated surface (i) has a coverage of 2 ML O and 2 ML H while the reduced surface (ii) has a coverage of 1.75 ML O and 1.5 ML H. For easy readability, those surfaces are numerated by (i) and (ii).

In principle, ALD reactions can be studied using ab-initio MD simulation (AIMD). However, ALD reactions fall into the category of rare events. This means that the system is trapped in some local energy minimum for a long period of time (relative to the AIMD time-scale) and cannot cross the activation barrier to a new minimum³⁸. We therefore tried out other plausible states (candidate minimums) by hand and checked stability with optimization or ab initio MD. Occasionally, chemical reactions occurred rapidly from the chosen configurations and were observed during optimization or MD. In those cases, we then looked for pathways showing how the system reached those configurations.

In this study, we use the nudged elastic band (NEB)³⁹⁻⁴⁰ method with climbing option to calculate the activation energy for ALD reactions under different OH-coverage. We therefore calculated the possible crossings of barriers by the NEB method and checked the activation barrier of a chemical reaction for different OH-coverages.

A major concern is the accuracy of activation energies, which affects the growth rate by ALD. There is a systematic error due to the approximate DFT exchange correlation functional that often results in underestimation of activation energies for breaking and making bonds. This can in principle be overcome by using more accurate methods⁴¹⁻⁴² rather than DFT. However, owing to the complicated reaction pathways that may result from densification¹⁹ or cooperative effects^{27, 43-44}, considering large cells with many atoms (e.g., here, 300 atoms with more than 1500 valence electrons) is necessary. This is too computationally demanding for the more accurate methods. Hence, at the present time, we rely on the activation energies calculated using DFT.

The energy difference between two optimized minima gives the reaction energy. Once the required minimum energy to cross the barrier is detected on the association or dissociation channel, this value is reported as the activation barrier. In contrast, occasionally no activation barrier is detected. In this case, we set the activation barrier to zero for an exothermic reaction, and to ΔE for an endothermic reaction. In all calculations, all other degrees of freedom are optimized.

The number of considered images for proton transfer and dissociation of H_2S is set to 10 in those reaction pathways while the number of images for desorption of protonated ligand has been increased to 14. This includes end images. The linear interpolation is utilized for the initial reaction pathway to find minimum energy path (corresponding to energy barriers). Special care is required on the construction of the initial reaction pathway on the complicated chemical reactions.

The vibrational frequencies of the systems are calculated within the harmonic approximation in order to include the zero point energy corrections (ZPE). ZPE contributions are found to be essential to describe the kinetics of atomic hydrogen⁴⁵⁻⁴⁶. The vibrational analysis has been performed for the initial state, transition state, and final state. The matrix of the second derivatives of the energy with respect to the atomic positions (Hessian matrix) is calculated numerically by displacing each atom twice (± 0.015 Å) independently from its equilibrium position in the direction of each Cartesian coordinate. The atoms involved in a chemical reaction are included in the frequency calculation. Often, the calculated activation energy is low (<0.1 eV) and the inclusion of ZPE contribution make the activation energy slightly negative. In those situations, the zero activation energy is reported (barrier-less reaction).

In this contribution, for the sake of simplicity and clearance, the dimethylamido ligand and the tert-butylimido ligand are shown by $X = N(CH_3)_2$ and $Y = NC(CH_3)_3$, respectively (see figure 1a). In this sense, desorbed HX is dimethylamine and the desorbed H_2Y is tert-butylamine.

To compute ab initio thermodynamics, the translational and vibrational entropy (S) of gas-phase molecules are numerically calculated⁴⁷ under the assumption that vibrational and surface contributions to S are approximately constant⁴⁸. TS^{transl} and TS^{rotat} at $T = 500$ K and 298.15 K are calculated for MoX_2Y_2 , HX, H_2Y and H_2S . This allows Gibbs free energies ΔG of the reactions to be reported step by step. The Gibbs free energy difference between two states is calculated as

$$\Delta G = \Delta(E_{elec} + E_{zpe}) - T\Delta S \quad (1)$$

Where the E_{elec} and E_{zpe} is the electronic and zero-point energy of a state, respectively. ΔS is the change in entropy between two states.

In proton transfer, not all proton transfer necessarily gives rise to the ligand desorption. If a proton transfer gives rise to the formation of a closed shell molecule, it may terminate in the desorption of the closed shell molecule. In the context of atomic orbitals, a closed shell configuration is a valence shell which is completely filled with electrons. In contrast, an open shell configuration is not completely filled with electrons. If a proton transfer gives rise to the formation of an open shell molecule, the formed molecule remains as an adsorbate. Proton transfer from a terminal OH group to N of the X ligand gives rise to the formation of HX, which is a closed shell molecule. However, proton transfer from the terminal OH group to nitrogen of the Y ligand gives rise to the formation of HY, which is an open shell molecule. Hence, the second proton transfer to the HY ligand is required to form a H_2Y molecule which has a closed shell molecule.

To include vdW interaction, the vdW functionals ‘optPBE-vdW’⁴⁹⁻⁵⁰ has been chosen to treat the reaction energy of the ALD reaction of MoS_2 at the SiO_2 surface, since there is good agreement between the vdW functionals (opt) and the random phase approximation (RPA) calculation⁵¹⁻⁵². The reaction energies are reported in separate tables in the SI.

Results and discussion

The ALD reactions that are included in the thermal process are the adsorption of precursors, proton transfer to ligands, desorption of the protonated ligands, densification of precursor, cooperative effects, and ultimately formation of dense atoms at the surface. The ALD reactions should ultimately hinder further precursor adsorption at the end of each pulse which gives rise to the self-limiting chemistry of ALD. This means that at the beginning of each pulse, the main course of chemical reactions are exothermic.

By consumption of surface-bound protons at the surface and reduction of reactive sites, the chemical reactions become endothermic and are less likely to proceed.

Each subsection begins with a short introduction, which is followed by the results of the calculations and ends with a short summary.

Start of MoX_2Y_2 pulse

Adsorption of MoX_2Y_2 precursor. In principle, the surface of a metal oxide has low coordinated terminal OH groups and terminal oxygen which are the chemically reactive sites. These reactive sites are Lewis basic oxygen sites, which can make a chemical bond by electron donation to the metal of the precursor molecule. The $\text{SiO}_2(0001)$ surface has reactive oxygen sites either with 1 or 2 coordination number (c.n.) (excluding H). In our model, the fully hydroxylated surface (i) has only terminal OH groups with 1 c.n. as reactive site (see figure 1a) while the reduced surface (ii) has different reactive sites. Those reactive sites are displayed as terminal OH groups, terminal oxygen, bridging OH groups, and bridging oxygen (see figure 1b).

Our calculation shows that the MoX_2Y_2 precursor cannot bond to the bridging oxygen. Similarly, other oxygen with same c.n. are therefore inaccessible to the metal of the precursor. The introduction of MoX_2Y_2 precursor to the fully hydroxylated surface (i) is depicted in figure 1a. No chemical bond is formed between Mo atom and terminal OH group on the fully hydroxylated $\text{SiO}_2(0001)$ surface (i). The adsorption is an endothermic reaction by 0.13 eV (Table 1, reaction 1). Similarly, introduction of MoX_2Y_2 precursor to terminal OH group at the reduced surface (ii) does not give rise to chemical adsorption. This terminates to the physisorbed precursor at the surface which is an exothermic reaction by 0.37 eV (Table 1, reaction 2).

However, the introduction of MoX_2Y_2 to the terminal O at the reduced surface (ii) gives rise to the formation of a chemical bond between Mo and terminal O. This chemical adsorption is an exothermic reaction by 1.79 eV which is associated with two proton transfer from terminal OH group to nitrogen (Table 1, reaction 3). The bond length between Mo and O is 2.10 Å.

Figure 1. Introduction of MoX_2Y_2 molecule onto the $\text{SiO}_2(0001)$ surface. (a) No chemical bond is formed between Mo and OH group at the fully hydroxylated $\text{SiO}_2(0001)$ surface (i). $\text{X}=\text{N}(\text{CH}_3)_2$ and $\text{Y}=\text{NC}(\text{CH}_3)_3$ ligands are shown by brown and green atoms, respectively. (b) Chemical adsorption of MoX_2Y_2 molecule onto O terminated at the reduced $\text{SiO}_2(0001)$ surface (ii). The chemical adsorption gives rise to the associated proton transfer from the terminal OH groups to the nitrogen (pink atoms). Terminal OH group, terminal oxygen, bridging OH group, and bridging oxygen are identified by yellow, black, green, and orange atoms, respectively (red=O, white=H, light gray=Si, dark gray=C, light blue=Mo, dark blue=N).

Barrier-less proton transfer from the terminal OH group to the N of X ligand is observed during the MoX_2Y_2 adsorption onto the reduced $\text{SiO}_2(0001)$ surface (ii). This implies that the rate of proton transfer to the X ligands should be high. Indeed, the calculated activation energy for proton transfer from terminal OH group to nitrogen shows that the values are below 0.5 eV. The proton transfer from terminal OH groups creates the chemically reactive terminal oxygen to forge a chemical bond to Mo of the precursor.

Chemical adsorption of MoX_2Y_2 onto $\text{SiO}_2(0001)$ surface does not occur at the terminal OH group at the surface. The Lewis basicity of the terminal OH and Lewis acidity of MoX_2Y_2 is not strong enough to give rise to chemical adsorption of precursor. The entropy change in the adsorption of MoX_2Y_2 is 0.98 eV at 298.15 K and is 1.74 eV at 500 K. The entropic effect makes the adsorption free energy more positive. In the following section, we will explain how the MoX_2Y_2 chemically bonds to terminal O due to proton transfer to the X ligand.

Proton transfer. In a previous study¹⁹, it was shown that the multiple protons transfer to dimethylamido ligands of the HfX_4 precursor takes place before desorption of dimethylamine. The calculated activation energy showed that repeated proton transfer from the surface to the X ligand and rotation of the protonated ligands is more energetically accessible than the simple desorption of dimethylamine amine in the initial stage. Due to multiple proton transfer to the ligands, the bond strength between Hf and N are weakened. This reduction in bond strength facilitates the desorption of dimethylamine from the precursor. The resulting activation energies for protonation and desorption of protonated ligands are low enough that these reactions can take place in low temperature ALD.

In the current case, proton transfer from the terminal OH group to N of X ligand gives rise to the chemical adsorption of physisorbed MoX_2Y_2 precursor at the fully hydroxylated surface (i) and formation of HX (figure 2a to 2c). This proton transfer is endothermic reaction by 0.42 eV and an activation energy of 0.65 eV is calculated for the first proton transfer (Table 1, reaction 4). After proton transfer, Mo forges a chemical bond to the terminal O. Due to proton transfer (pink atom), proton diffusion is observed at the $\text{SiO}_2(0001)$ surface (green atom) and the bond length between Mo and N is increased from 2.05 to 2.35 Å.

The second proton transfer is an exothermic reaction by 0.18 eV. A zero activation energy is calculated for the second proton transfer (Table 1, reaction 5). Similarly, the proton diffusion is observed during the course of proton transfer from terminal OH group to N of X (figure 2d to 2f). Due to proton transfer, the bond length between Mo and N is increased from 2.07 Å to 2.23 Å.

The same calculations have been done for the reduced surface (ii). An activation energy of 0.04 eV is calculated for the first proton transfer from terminal OH group to the physisorbed precursor (Table 1, reaction 6). This reaction is endothermic by 0.04 eV. Owing to proton transfer, the bond length between Mo and N is increased from 2.05 Å to 2.13 Å.

In the following step, the physisorbed MoHX_2Y_2 precursor chemically bonds to the terminal O. This reaction is exothermic by 0.25 eV and activation energy of 0.15 eV is calculated for the chemisorption of protonated precursor (Table 1, reaction 7). Due to the formation of chemical bond between Mo and O, the bond length between Mo and N is increased from 2.13 Å to 2.38 Å.

The second proton transfer at the reduced surface (ii) is an exothermic reaction by 0.07 eV. A zero activation energy is calculated for the second proton transfer at the reduced surface (ii) (Table 1, reaction 8). Due to proton transfer, the bond length between Mo and N is increased from 2.06 Å to 2.26 Å.

Proton transfer from a terminal OH group surface to N of X increases the Lewis basicity of the formed terminal O and Lewis acidity of protonated MoX_2Y_2 , which gives rise to chemical adsorption of the protonated precursor. In this picture, metal precursor is initially only physically adsorbed to the surface and proton transfer from surface to the ligands gives rise to chemical adsorption of metal precursor.

Figure 2. Proton transfer from terminal OH group to N of X ligand. The MoX_2Y_2 is chemically bound onto the fully hydroxylated surface (i) due to proton transfer (a) to (c). (a) Initial configuration of the physisorbed MoX_2Y_2 molecule. (b) Transition state. (c) Proton transfer gives rise to the formation of chemical bond between Mo and O. Second proton transfer makes the chemisorption more favorable (d) to (f). (d) Initial configuration of the chemisorbed MoHX_2Y_2 molecule. (e) Transition state. (f) Proton transfer from the surface terminal OH group to the N of ligands weakens the bonds between Mo and N. Pink and green atom shows the transferred proton between O and N and the diffused proton between O atoms, respectively (the color code is the same as figure 1).

Before desorption of dimethylamine, proton transfer to Y ligand does not occur. The transferred proton to Y ligand does not chemically bond to the nitrogen. In the case of HfX_4 , all ligands of precursor are symmetrical. Hence, multiple proton transfer reduces the strength of bond between Hf and N which gives rise to facilitative desorption of dimethylamine. However, in the case of MoX_2Y_2 , ligands are less symmetrical and higher number of proton transfer is required to reduce the bond strength between Mo-N. Hence, the reaction pathway of multiple proton transfer will be hindered in the case of MoX_2Y_2 .

Proton transfer to the remaining precursor continues to take place after dimethylamine desorption. Proton transfer to the MoXY_2 is depicted in figure 3a to 3c. This reaction is exothermic by 0.04 eV and a zero activation energy is calculated by NEB method (Table 1, reaction 9). Proton transfer (pink atom) modifies the Lewis basicity of terminal O which gives rise to the proton diffusion from neighboring terminal OH group to the terminal O (green atom). This can be accounted as associated proton diffusion to the original proton transfer.

Figure 3. Proton transfer to the remaining ligands. Proton transfer from terminal OH at the fully hydroxylated surface (i) to the MoXY_2 is depicted from (a) to (c). (a) Shows the initial configuration of MoXY_2 (b) Transition state (c) the formation of HX. Associated proton diffusion is observed during the course of proton transfer (green atom). Proton transfer to the nitrogen of Y ligand is shown from (d) to (f). (d) Shows the initial configuration of MoY_2 . Mo has 4 c.n. in this configuration. (e) Transition state. (f) Due to proton transfer from terminal OH group, O makes a chemical bond with Mo. In this configuration, Mo has c.n. of 5.

Table 1. Adsorption energies of MoX_2Y_2 and activation energy of proton transfer for different OH-coverages.

Reaction	OH-coverage	E_a (eV)	ΔE (eV)	$\Delta G^{500\text{K}}(\Delta G^{298\text{K}})$ (eV)	Reactive site involved in reaction
1. $\text{MoX}_2\text{Y}_2(\text{g}) \rightarrow \text{MoX}_2\text{Y}_2^*$	2 ML O and 2 ML H		+0.13	+1.87 (+1.11)	Terminal OH
2. $\text{MoX}_2\text{Y}_2(\text{g}) \rightarrow \text{MoX}_2\text{Y}_2^*$	1.75 ML O and 1.50 ML H		-0.37	+1.37 (+0.61)	Terminal OH
3. $\text{MoX}_2\text{Y}_2(\text{g}) + 2\text{OH}(\text{s}) \rightarrow \text{MoH}_2\text{X}_2\text{Y}_2(\text{s}) + 2\text{O}(\text{s})$	1.75 ML O and 1.50 ML H		-1.79	-0.05 (-0.80)	Terminal O
4. $\text{MoX}_2\text{Y}_2^* + \text{OH}(\text{s}) \rightarrow \text{MoHX}_2\text{Y}_2(\text{s}) + \text{O}(\text{s})$	2 ML O and 2 ML H	0.65	+0.42	+2.16 (+1.40)	Terminal OH
5. $\text{MoHX}_2\text{Y}_2(\text{s}) + \text{OH}(\text{s}) \rightarrow \text{MoH}_2\text{X}_2\text{Y}_2(\text{s}) + \text{O}(\text{s})$	2 ML O and 2 ML H	0.00	-0.18	---	Terminal OH
6. $\text{MoX}_2\text{Y}_2^* + \text{OH}(\text{s}) \rightarrow \text{MoHX}_2\text{Y}_2^* + \text{O}(\text{s})$	1.75 ML O and 1.50 ML H	0.04	+0.04	+1.78 (+1.02)	Terminal OH
7. $\text{MoHX}_2\text{Y}_2^* \rightarrow \text{MoHX}_2\text{Y}_2(\text{s})$	1.75 ML O and 1.50 ML H	0.15	-0.25	+1.49 (+0.73)	Terminal O
8. $\text{MoHX}_2\text{Y}_2(\text{s}) + \text{OH}(\text{s}) \rightarrow \text{MoH}_2\text{X}_2\text{Y}_2(\text{s}) + \text{O}(\text{s})$	1.75 ML O and 1.50 ML H	0.00	-0.07	---	Terminal OH
9. $\text{MoXY}_2(\text{s}) + \text{OH}(\text{s}) \rightarrow \text{MoHXY}_2(\text{s}) + \text{O}(\text{s})$	2 ML O and 2 ML H	0.00	-0.04	---	Terminal OH
10. $\text{MoY}_2(\text{s}) + \text{OH}(\text{s}) \rightarrow \text{MoHY}_2 + \text{O}(\text{s})$	2 ML O and 2 ML H	0.60	-0.16	---	Terminal OH
11. $\text{MoY}_2(\text{s}) + \text{OH}(\text{s}) \rightarrow \text{MoHY}_2 + \text{O}(\text{s})$	1.75 ML O and 1.50 ML H	0.00	-1.56	---	Bridging OH
12. $\text{MoY}_2(\text{s}) + \text{OH}(\text{s}) \rightarrow \text{MoHY}_2 + \text{O}(\text{s})$	1.75 ML O and 1.50 ML H	0.52	+0.49	---	Terminal OH
13. $\text{O}(\text{s}) + \text{OH}(\text{s}) \rightarrow \text{OH}(\text{s}) + \text{O}(\text{s})$	1.75 ML O and 1.50 ML H	0.22	-1.83	---	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).

Once two dimethylamines desorbed from the surface, the Mo of the remaining precursor is densified to the surface. Mo chemically forges two bonds to the terminal O (figure 3d). In this situation, since the distance between Y ligand and terminal OH group has

been reduced and Mo chemically bonds to the terminal O, proton transfer to Y ligand can occur. A relatively large activation energy of 0.60 eV is calculated for proton transfer from the fully hydroxylated surface (i) to Y ligand. The proton transfer is exothermic reaction by 0.16 eV (Table 1, reaction 10). As depicted in figure 3d to 3f, due to proton transfer from a terminal OH group to the N of Y ligand, Mo obtains a higher c.n. of 5 and the bond length between Mo and N is increased from 1.74 Å to 1.89 Å. Terminal OH groups do not give the second proton to the HY ligand. This indicates that the transferred proton to N of HY (by hand) does not chemically bond to N and it is not a plausible configuration in this stage.

The same calculations have been done for the proton transfer to Y ligand at the reduced surface (ii) of SiO₂(0001). As described above, there are various reactive sites at the reduced surface (ii). The terminal OH group and bridging OH group are two possible reactive sites for proton transfer. A zero activation energy is calculated for proton transfer from a bridging OH group to the N of Y ligand. This reaction is exothermic by 1.56 eV (Table 1, reaction 11). In contrast, a large activation energy of 0.52 eV is calculated for proton transfer from terminal OH group to Y ligand. This reaction is endothermic by 0.49 eV. This indicates that even if the Y ligand becomes protonated due to proton transfer from a bridging OH group, it would easily be deprotonated due to proton transfer from HY ligand to the terminal O group. The reaction of deprotonation is an exothermic reaction by 0.49 eV and has an activation energy of 0.03 eV (the reverse of reaction 12, Table 1). The activation energy of 0.22 eV is calculated for proton transfer from a bridging OH group to terminal O. Bridging OH has c.n. of 2 while terminal O has c.n. of 1. This reaction is exothermic by 1.83 eV (Table 1, reaction 13).

Proton transfer from a terminal OH group to the N of X is a favorable reaction on both surfaces. This facilitates the chemical adsorption of the protonated MoX₂Y₂ precursor and desorption of dimethylamine on both surfaces. During the course of proton transfer, coupled proton diffusion is observed at the surface. In contrast, proton transfer from a terminal OH group to the N of Y is not an entirely favorable reaction. The fully hydroxylated surface (i) does not have enough Lewis basic sites (terminal OH groups) to protonate the Y ligand entirely, giving rise to the desorption of tert-butylamine. Thus, Y ligands can only be partially protonated at the fully hydroxylated surface (i). During the H₂S pulse we will show how this is vital to cause tert-butylamine desorption. Protonation of the Y ligand on the reduced surface (ii) is an entirely unfavorable reaction. Reduction of the surface will diminish the strength of Lewis basicity towards the MoX₂Y₂ precursor and deactivate the ALD reactions.

Desorption of HX ligands and densification of metal precursor. The activation energy for desorption of an open shell molecule is large. A large activation energy (>2.0 eV) is calculated for desorption of an X or Y ligand. If an open shell fragment of a molecule dissociates from its molecule, the self-limiting feature of ALD will not be kept anymore since the remaining precursor is chemically reactive and the course of reactions will not follow the dominant reaction pathways of ALD. Hence, it terminates with the loss of conformality and stoichiometry of the thin film.

After proton transfer, the HX fragment is a closed shell molecule. In this situation, desorption of HX is often the energetically favorable reaction. Desorption of the first dimethylamine from MoH₂X₂Y₂ at the fully hydroxylated surface (i) is shown in figure (4a to 4c). This reaction is exothermic by 0.63 eV and an activation energy of 0.37 eV is calculated for desorption of dimethylamine (Table 2, reaction 1).

Desorption of the second HX from MoHXY₂ at the fully hydroxylated surface (i) is also an exothermic reaction by 0.21 eV. A large activation energy of 1.05 eV is calculated for desorption of the second dimethylamine (Table 2, reaction 2). During the course of densification, Mo chemically bonds to the terminal OH group, which leads to proton diffusion to the neighboring oxygen (green atom). The entropy change in the desorption of HX is 0.76 eV at 298.15 K and is 1.37 eV at 500 K. The entropic effect makes the desorption free energy more negative.

Typically, during steady state deposition (homodeposition), through desorption of the second ligand of a symmetrical precursor like HfX₄, TMA, and HfCl₄, the remaining precursor would be densified into the surface²⁷. Through densification, a large amount of energy is released due to bond formation between metal precursor and existing oxygen at the surface.

In contrast, densification of MoX₂Y₂ into the SiO₂(0001) surface is not as exothermic as densification of the mentioned metal precursors during homodeposition. The densification of MoY₂ is poor in the bond formation between Mo and O. In this situation, the Mo forges two chemical bonds to terminal O at the surface. The chemical bond between Mo and N of Y ligand is stronger than the chemical bond between Mo and N of X ligand. Hence, the remaining ligands would less likely allow that the Mo comes to the surface and bond to more terminal O at the surface. Hence, in the case MoX₂Y₂, the released energy due to densification of metal precursor is an order of magnitude smaller than densification of metal precursor in homodeposition.

Similarly, the reaction energy and activation energy of desorption of dimethylamine are calculated for the reduced surface (ii). As tabulated in (Table 2, reaction 3), the first desorption is exothermic reaction by 0.27 eV but it is not as exothermic as the equivalent reaction in fully hydroxylated surface (i) (Table 2, reaction 2). An activation energy of 0.64 eV is calculated for the first desorption. An activation energy of 1.06 eV is calculated for the second desorption which is similar to the equivalent reaction in the fully hydroxylated surface (i) (Table 2, reaction 4). However, this reaction is endothermic by 0.57 eV. Hence, densification is an endothermic reaction at the reduced surface (ii).

Desorption of dimethylamine and densification of MoX₂Y₂ precursor onto the reduced surface (ii) is not as favorable as onto the fully hydroxylated surface (i). Since the number of terminal OH groups has been reduced, the chemical reactivity of surface to absorb the metal precursor has been reduced. Hence, in heterodeposition the chemical reactivity of surface is identified by OH coverage. Proton is required to form the closed shell ligand and the terminal oxygen is required to be replaced by desorbed ligand.

Figure 4. Desorption of the protonated ligand. Desorption of the first dimethylamine group is depicted from (a) to (c). (a) Shows the initial configuration of adsorbed $\text{MoH}_2\text{X}_2\text{Y}_2$ at the fully hydroxylated surface (i). (b) Transition state. (c) Desorption of dimethylamine and formation of MoHXY_2 at the surface. The transferred proton is identified by pink atom. The second desorption of dimethylamine is shown from (d) to (f). (d) The initial configuration of MoHXY_2 . (e) Transition state. (f) Through desorption of dimethylamine, the remaining precursor of MoY_2 is densified to the surface. During the course of densification, Mo forges a chemical bond to O and proton diffusion is observed to the neighboring O (green atom).

After densification of remaining precursor, the calculated activation energy for proton transfer from terminal OH group to N of Y ligand is large (Table 1, reaction 10). Even if H_2Y is formed, activation energy for tert-butylamine desorption is larger than 4.61 eV. Hence, the densified MoY_2 is energetically most probable configuration at the end of metal pulse and depending on the proton coverage in the vicinity of the densified precursor, Y ligands are protonated to some extent.

Table 2. Activation energy and reaction energy of H_2S adsorption, H_2S dissociation, and desorption of protonated ligands.

Reaction	OH-coverage	E_a (eV)	ΔE (eV)	$\Delta G^{500\text{K}}(\Delta G^{298\text{K}})$ (eV)	Initial c.n. of Mo
1. $\text{MoH}_2\text{X}_2\text{Y}_2(\text{s}) \rightarrow \text{MoHXY}_2(\text{s}) + \text{HX}(\text{g})$	2 ML O and 2 ML H	0.37	-0.63	-2.00 (-1.93)	c.n.=5
2. $\text{MoHXY}_2(\text{s}) \rightarrow \text{MoY}_2(\text{s}) + \text{HX}(\text{g})$	2 ML O and 2 ML H	1.05	-0.21	-1.58 (-0.97)	c.n.=4
3. $\text{MoH}_2\text{X}_2\text{Y}_2(\text{s}) \rightarrow \text{MoHXY}_2(\text{s}) + \text{HX}(\text{g})$	1.75 ML O and 1.50 ML H	0.64	-0.27	-1.64 (-1.03)	c.n.=5
4. $\text{MoHXY}_2(\text{s}) \rightarrow \text{MoY}_2(\text{s}) + \text{HX}(\text{g})$	1.75 ML O and 1.50 ML H	1.06	+0.57	-0.80 (-0.19)	c.n.=4
5. $\text{MoHY}_2(\text{s}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{MoHY}_2(\text{s}) + \text{H}_2\text{S}(\text{s})$	2 ML O and 2 ML H		-0.17	+0.97 (+0.46)	c.n.=5
6. $\text{MoHY}_2(\text{s}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{MoH}_2\text{Y}_2(\text{s}) + \text{SH}(\text{s})$	2 ML O and 2 ML H	0.59	-0.29	+0.85 (+0.34)	c.n.=5
7. $\text{MoY}_2(\text{s}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{MoY}_2(\text{s}) + \text{H}_2\text{S}(\text{s})$	1.75 ML O and 1.50 ML H		+0.11	+1.25 (+0.74)	c.n.=4
8. $\text{MoHY}_2(\text{s}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{MoHY}_2(\text{s}) + \text{H}_2\text{S}(\text{s})$	1.75 ML O and 1.50 ML H		-0.26	+0.88 (+0.36)	c.n.=4
9. $\text{MoY}_2(\text{s}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{MoHY}_2(\text{s}) + \text{SH}(\text{s})$	1.75 ML O and 1.50 ML H	0.80	-0.34	+0.80 (+0.28)	c.n.=4
10. $\text{MoH}_3\text{Y}_2(\text{s}) \rightarrow \text{MoHY}(\text{s}) + \text{H}_2\text{Y}(\text{g})$	2 ML O and 2 ML H	0.29	-0.04	-1.51 (-0.86)	c.n.=6
11. $\text{MoHY}(\text{s}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{MoH}_2\text{Y}(\text{s}) + \text{H}_2\text{S}^*$	2 ML O and 2 ML H		+0.14	+1.28 (+0.77)	c.n.=5
12. $\text{MoHY}(\text{s}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{MoH}_2\text{Y}(\text{s}) + \text{SH}(\text{s})$	2 ML O and 2 ML H	1.09	+0.04	+1.51 (+0.86)	c.n.=5
13. $\text{MoH}_2\text{Y}(\text{s}) \rightarrow \text{Mo}(\text{s}) + \text{H}_2\text{Y}(\text{g})$	2 ML O and 2 ML H	0.79	+0.31	-1.16 (-0.51)	c.n.=6
14. $\text{MoH}_2\text{Y}(\text{s}) + \text{H}_2\text{S}(\text{g}) \rightarrow \text{MoH}_2\text{Y}(\text{s}) + \text{H}_2\text{S}(\text{s})$	2 ML O and 2 ML H		-0.03	+1.11 (+0.60)	c.n.=6
15. $\text{MoH}_2\text{Y}(\text{s}) \rightarrow \text{Mo}(\text{s}) + \text{H}_2\text{Y}(\text{g})$	2 ML O and 2 ML H	0.35	-1.41	-2.88 (-2.23)	c.n.=7

16. $\text{H}_2\text{S}^* + \text{OH}(\text{s}) \rightarrow \text{SH}(\text{s}) + \text{OH}(\text{s})$	2 ML O and 2 ML H	0.00	-0.95	---	---
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* Shows the physisorbed precursor. Gibbs free energy ΔG are given in two different temperatures $T = 500 \text{ K}$ and $T = 298.15 \text{ K}$ (in parenthesis).

Start of H_2S pulse

During the heterodeposition of MoS_2 on a $\text{SiO}_2(0001)$ surface two MoY_2 are less likely to be located beside each other due to steric effects. Hence, the remaining MoY_2 cannot cooperate in adsorption or dissociative adsorption of H_2S and consequently the “cooperative effect” reaction pathway between the densified precursors²⁷ is hindered in heterodeposition of MoS_2 .

Adsorption and dissociation of H_2S and desorption of H_2Y ligands. During the subsequent pulse, H_2S chemically reacts with the remaining precursor at the surface. In our calculation, H_2S is introduced one by one to the remaining precursor. H_2S is often chemically adsorbed to the remaining precursor and forges a chemical bond to Mo, or H_2S is only physically adsorbed and no chemical bond is observed between Mo and S. In both cases, dissociation of H_2S to SH and H is calculated afterwards.

H_2S bonds chemically to MoHY_2 on the fully hydroxylated surface (i) (figure 5a). The adsorption is exothermic by 0.17 eV (Table 2, reaction 5). Due to steric effects, the introduction of a second H_2S does not give rise to any adsorption. In the following step, dissociation of H_2S to SH and H is calculated. During the course of H_2S dissociation, H transfers to N of the HY ligand and forms H_2Y while a SH group is chemically bound to Mo (figure 5a to 5c). An activation energy of 0.59 eV is calculated for dissociation of H_2S by the remaining precursor. The reaction is exothermic by 0.29 eV (Table 2, reaction 6). Due to H_2S dissociation, the bond length between Mo and N is increased from 1.91 Å to 2.29 Å and the bond length between Mo and S is reduced from 2.70 Å to 2.36 Å. The entropy change in the adsorption of H_2S is 0.63 eV at 298.15 K and is 1.14 eV at 500 K. The entropic effect makes the adsorption free energy more positive.

Figure 5. Dissociation of H_2S to SH and H on the densified MoHY_2 at the fully hydroxylated surface (i) (a) to (c). (a) Shows the initial configuration of MoHY_2 and the chemisorbed H_2S . (b) Transition state. (c) Dissociation of H_2S to thiol group and proton. Proton transfer gives rise to the formation of H_2Y while SH chemically bonds to Mo. Dissociation of H_2S to SH and H at the densified MoY_2 at the reduced surface (ii) (d) to (f). (d) Shows the initial configuration of MoY_2 and the chemisorbed H_2S . (e) Transition state. (f) The formation of HY and SH due to the proton transfer to Y ligand (red=O, white=H, light gray=Si, dark gray=C, light blue=Mo, dark blue=N, yellow=S).

Similar calculations have been done for the H_2S dissociation on the densified MoY_2 at the reduced surface (ii). The introduction of H_2S gives rise to the formation of a chemical bond between S and Mo (figure 5d). The chemisorption of H_2S is endothermic by 0.11 eV (Table 2, reaction 7). Similarly, adsorption of H_2S on the densified MoHY_2 at the reduced surface (ii) is an exothermic reaction by 0.26 eV (Table 2, reaction 8). This indicates that owing to proton transfer to the Y ligand, the adsorption of H_2S becomes a more favorable reaction. In the following step, the activation energy of H_2S dissociation to SH and H is calculated on the densified MoY_2 at the reduced surface (ii) (figure 5d to 5f). An activation energy of 0.80 eV is calculated and this reaction is exothermic by 0.34 eV (Table 2, reaction 9). The bond length between Mo and N is increased from 1.77 Å to 1.91 Å and the bond length between Mo and S is reduced from 2.66 Å to 2.38 Å, during the course of H_2S dissociation on the densified MoY_2 .

Adsorption of H_2S is facilitated on the densified precursor with protonated ligands. Protonation of Y ligands improves the Lewis acidity of Mo and basicity of N and facilitates dissociation of H_2S . Dissociation of H_2S on the densified precursor with protonated ligands is more energetically favorable than on non-protonated ligands. The formed thiol group resulting from the dissociation of

H_2S does not give another proton to the N of the Y ligand. Hence, it is crucial that the proton that was transferred to the Y ligand is partially supplied by terminal OH groups from the surface, otherwise the formation of H_2Y in the H_2S pulse does not proceed any more and consequently Y ligands remain at the surface. The remaining ligands will de-activate the ALD reactions, which gives rise to delay in the nucleation of the thin-film.

As shown above, the rate of proton transfer at the reduced surface (ii) is much lower than at the fully hydroxylated surface (i). Hence, it is less likely that protonated MoY_2 is formed at the reduced surface (ii) and subsequently dissociation of H_2S is de-activated and ALD reactions of tert-butylamine desorption are hindered at the reduced surface (ii). Therefore, in the following discussion, we only investigate desorption of tert-butylamine from the fully hydroxylated surface (i).

Figure 6. Desorption of tert-butylamine and dissociative adsorption of H_2S on MoHY at the fully hydroxylated surface (i). Desorption of the first tert-butylamine from the remaining precursor is depicted from (a) to (c). (a) Show the initial configuration of MoH_3Y_2 at the surface. The H_2Y fragment is formed and Mo has c.n. of 5. (b) Transition state. (c) The tert-butylamine is desorbed and is replaced by a thiol group (ligand exchange). Dissociative adsorption of H_2S is shown from (d) to (f). (d) Shows the initial configuration of MoHY. H_2S molecule is only physically adsorbed to the remaining precursor. (e) Transition state. (f) H_2Y fragment is formed and thiol group forges a chemical bond to Mo.

Due to the proton transfer and dissociation of H_2S , H_2Y fragments can be formed on the fully hydroxylated surface (i). This is depicted in figure 6a. In this configuration, Mo has 6 c.n. An activation energy of 0.29 eV is calculated for tert-butylamine desorption (Table 2, reaction 10). This reaction is exothermic by 0.04 eV. Due to tert-butylamine desorption, a thiol group is relocated to the position of desorbed H_2Y (figure 6a to 6c). Desorption of tert-butylamine opens more space for adsorption of the next H_2S molecules. The entropy change in the desorption of H_2Y is 0.82 eV at 298.15 K and is 1.47 eV at 500 K. The entropic effect makes the desorption free energy more negative.

The introduction of the next H_2S molecule to the remaining MoHY does not give rise to the formation of a chemical bond between Mo and S. The H_2S is only physically adsorbed to the remaining precursor of MoHY (figure 6d). This reaction is endothermic by 0.14 eV (Table 2, reaction 11). Next, a large activation energy of 1.09 eV is calculated for dissociative adsorption of physisorbed H_2S . This reaction is endothermic by 0.04 eV (Table 2, reaction 12). Through the course of dissociative adsorption of H_2S , a thiol group forges a chemical bond to Mo and H_2Y is formed. Due to the dissociative adsorption of H_2S on MoHY, the bond length between Mo and N is increased from 1.89 Å to 2.27 Å and the bond length between Mo and S is reduced from 2.97 Å to 2.43 Å.

As depicted in figure 7a, the closed shell molecule of H_2Y is formed. In this configuration, Mo has a c.n. of 6. An activation energy of 0.79 eV is calculated for desorption of the second tert-butylamine. This desorption is endothermic by 0.31 eV (Table 2, reaction 13). Hence, dissociative adsorption of H_2S gives rise to the formation of H_2Y but desorption of a second tert-butylamine is still not energetically favorable.

Figure 7. A facile desorption of tert-butylamine due to the co-adsorption of multiple H_2S molecules (2 vs. 3 H_2S molecules). Desorption of a second tert-butylamine from MoH_2Y is shown at the fully hydroxylated surface (i) (a) to (c). (a) Shows the initial configuration of MoH_2Y . Mo has a c.n. of 6 in this configuration. (b) Transition state. (c) Due to desorption of tert-butylamine, a thiol group is relocated to the tert-butylamine position. Facilitative desorption of tert-butylamine from MoH_2Y is shown at the fully hydroxylated surface (i) (d) to (f). During the course of tert-butylamine desorption, the coupled dissociation of H_2S and proton diffusion occur. H_2S is dissociated to a neighboring OH group (green atoms) (d) Shows the initial configuration of MoH_2Y . Mo has c.n. of 7. (e) Transition state. (f) The second tert-butylamine is desorbed from the surface. Tert-butylamine desorption and relocation of the thiol group complete the ligand exchange and give rise to the formation of densified Mo with c.n. of 6.

Once H_2Y is formed, the introduction of the next H_2S molecule gives rise to chemical adsorption of H_2S (figure 7d). This reaction is exothermic by 0.03 eV (Table 2, reaction 14). In this configuration, Mo has c.n. of 7. The activation energy of 0.35 eV is calculated for desorption of the second tert-butylamine. The tert-butylamine desorption is an exothermic reaction by 1.41 eV (Table 2, reaction 15). The second desorption of tert-butylamine will lead to the coupled dissociation of H_2S to SH and H and proton diffusion at the surface (green atoms). A terminal OH group participates in the dissociation of H_2S and gives its proton to a neighboring terminal O. the bond length between Mo and S is reduced from 2.85 Å to 2.44 Å.

The large amount of released energy of 1.49 eV in desorption of the second tert-butylamine is due to the associated dissociation of H_2S . The released energy of 0.95 eV is calculated for the dissociation of H_2S before desorption of tert-butylamine (Table 2, reaction 16). Zero activation energy is calculated for the dissociation of H_2S before tert-butylamine desorption.

Co-adsorption of H_2S on the densified MoH_2Y is facilitated by protonated Y ligands. The Lewis acid site of Mo and Lewis base site of N and O cooperate to dissociate H_2S , which gives rise to the formation of H_2Y and desorption of tert-butylamine. This indicates that the increase of temperature and pressure induces a cooperative effect during the H_2S pulse, which facilitates the course of ligand exchange during the H_2S pulse.

Through the cooperative effects, H_2Y is desorbed and replaced by a thiol group. In this stage, the densified Mo has 3 c.n. from SH groups and 3 c.n. from terminal O at the surface (figure 7f). In this structure, the formed terminal SH groups, beside the neighboring terminal OH groups at the surface, act as reactive sites for the further adsorption of MoX_2Y_2 in the metal pulse, and are therefore nucleation sites in the following ALD cycles. The repeat of the above simulated ALD reactions would lead to the formation of similar structure at the surface. This ultimately terminates in the formation of a complete buffer-layer in which Mo atoms covalently bond to the S and O atoms at the interface.

Summary of the most important insights

In this paper, we use atomistic simulation at the DFT level to investigate the atomic layer deposition of MoS_2 from $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2/\text{H}_2\text{S}$ on the $\text{SiO}_2(0001)$ surface. We include the early stage of adsorption of each precursor in each pulse to the formation of densified atoms at the interface. The resulting reactions, which describe the fundamental chemistry of atomic layer deposition of 2D MoS_2 at the hydroxylated and reduced $\text{SiO}_2(0001)$ interfaces, are summarized below:

Adsorption of $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$

$\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ does not chemically bond to terminal OH groups at the $\text{SiO}_2(0001)$ surface. The Lewis basicity of the terminal OH is not strong enough to give rise to chemical adsorption of precursor. Alternatively, $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ precursor is only physically adsorbed to the surface and proton transfer from a terminal OH group to the ligand increases the Lewis basicity of termi-

nal O and Lewis acidity of Mo, which gives rise to the chemical adsorption of the metal precursor. The described picture of chemical adsorption of $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ on the $\text{SiO}_2(0001)$ surface is in contrast to the common knowledge of chemical adsorption of metal precursors and subsequent protonation of ligands. A summarizing, schematic diagram for chemical adsorption of the metal precursor is provided in Scheme 1.

Scheme 1. The changes observed in DFT calculations in the Lewis basicity (blue/green) and acidity (red/brown) of surface atoms during the adsorption of metal precursor on SiO_2 surface (M = metal, X and Y = ligands). ‘Strong’ and ‘Weak’ are meant as relative terms, as the absolute acidity or basicity depends on the particular system. Solid lines are indicative of chemical bond between elements and dashed line shows weak interaction. Proton transfer between physisorbed precursor and terminal OH group, gives rise to the chemical adsorption of metal precursor.

Proton transfer

Proton transfer from the terminal OH group surface to the N of dimethylamido ligand gives rise to the chemical adsorption of protonated precursor and consequently desorption of dimethylamine. However, proton transfer from terminal OH to Y ligand does not occur before desorption of dimethylamine. In this case, the reaction pathway of multiple proton transfers, which is typically the dominant reaction pathway in homodeposition of ALD, is deactivated for the heteroleptic $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ precursor, which delays the incubation period. In addition, we summarize the protolytic reaction of surface (i) and (ii) as below:

Protolytic reactivity of the fully hydroxylated surface (i): Proton transfer from terminal OH group to N of dimethylamido ligand is the favorable reaction. $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ precursor is previously chemisorbed to the surface. Proton transfer from a terminal OH group to N of tert-butylimido ligand is also chemically favorable reaction. However, this can only partially protonated tert-butylimido ligand at the fully hydroxylated surface, since the transferred second proton from the surface to the protonated tert-butylimido ligand does not chemically bond to N and it is not a plausible configuration. Therefore, tert-butylamine is less likely formed in this stage.

Protolytic reactivity of the reduced surface (ii): Proton transfer from terminal OH group to N of dimethylamido ligand is also the favorable reaction. $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ precursor is previously chemisorbed to the surface. In contrast, proton transfer from terminal OH to N of tert-butylimido ligand is not an entirely favorable reaction. Since the number of terminal OH groups has been reduced, the protolytic reactivity of the surface towards the metal has been reduced and longer incubation period than fully hydroxylated surface is expected.

H_2S Pulse

During the H_2S pulse, dissociation of H_2S on the partially protonated Y ligand gives rise to tert-butylamine desorption while this does not occur in the case of non-protonated Y ligand. Thus, the reduction of the surface will reduce the strength of Lewis basicity towards $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ and deactivates the ALD reactions.

Densification of MoY_2

Densification of the heteroleptic precursor of $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ onto the $\text{SiO}_2(0001)$ surface is not as exothermic as densification of the homoleptic metal precursor in homodeposition of ALD. The densification of MoY_2 is poor in the bond formation between Mo and O. The strong chemical bonds would less likely allow that the Mo comes to the surface and bond to more terminal O at the surface. Hence, the released energy due to densification of metal precursor is an order of magnitude smaller than densification of homoleptic metal precursor in homodeposition.

Desorption of protonated ligand

Desorption of dimethylamine from the metal precursor on the reduced surface is not as favorable as on the fully hydroxylated surface. In ALD reactions, a proton is required to form a closed shell ligand and a terminal oxygen is required to bond to the metal to replace the desorbed dimethylamine. Therefore, in heterodeposition of ALD, OH coverage identifies the chemical reactivity of the surface towards the metal precursor.

Protonation of Y ligands improves the Lewis acidity of Mo and basicity of N, which gives rise to the favorable adsorption and the facile dissociation of H_2S . Dissociation of H_2S on the densified precursor with protonated ligands is energetically more favorable than on the non-protonated ones. Hence, it is crucial that the protonation of Y ligand is partially supplied from the terminal OH groups from the surface, otherwise the formation of H_2Y in the H_2S pulse does not proceed anymore and consequently Y ligands remain at the surface. The remaining ligands will de-activate the ALD reactions, giving rise to delay in the nucleation of thin-film. Scheme 2. shows how the reduced surface can delay the incubation period in ALD.

Scheme 2. The success and delays in ALD deposition observed in DFT calculations. The calculated reaction energetics and reaction kinetics shows how the chemical reactions of ALD can effectively proceed. The initial coverage of reactive sites at the surface affects the success or delays in the formation of buffer layer. The color code is the same as Scheme 1.

Cooperative effect

An increase of temperature and an increase of H_2S pressure give rise to the increase of H_2S dissociation rate and the increase of impingement rate, respectively. This will activate a cooperative effect between H_2S molecules to protonate the Y ligands and gives rise to desorption of tert-butylamine. Through this reaction pathway, the remaining Y ligand will be replaced by a thiol group on Mo and the incubation period is shortened. A summarizing, schematic diagram for reaction pathway of ligand exchange in sulphur pulse is depicted in Scheme 3.

Scheme 3. The changes observed in DFT calculations in the Lewis basicity (blue/green) and acidity (red/brown) of H_2S dissociation and desorption of protonated ligand. Co-adsorption of H_2S molecules and dissociation of H_2S molecule by the neighboring Lewis base sites reduce the Lewis acidity of metal, give rise to the desorption of protonated ligands (cooperative effect in sulphur pulse). The color code is the same as Scheme 1.

Formation of buffer-layer:

Through the first ALD cycles, using $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ and H_2S , a fully coordinate Mo (c.n. = 6) with terminal SH groups at the $\text{SiO}_2(0001)$ surface is formed. The formation of such structure may take a long time since the heterodeposition has a slower reaction rate than homodeposition. In the following cycles, the terminal SH group could act as nucleation sites. These sites have lower coordination number and consequently higher chemical reactivity (Supporting Information (SI), Figure 1). Hence, the following ALD reactions are chemically facilitated gives rise to the formation of similar morphology at the surface. Ultimately, the buffer-layer would be completed in which the Mo atoms share covalent bonds with O and S at the interface (SI, Figure 2).

Conclusions

In summary, DFT simulations give insightful information on the early stages (heterodeposition) of ALD of 2D- MoS_2 using $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ and H_2S as precursors. A fully hydroxylated SiO_2 facilitates the ALD reactions, including the chemical adsorption of metal precursor, desorption of dimethylamine, densification of the metal precursor and partially protonation of tert-butylimido ligands. A high temperature and high H_2S partial pressure is essential to activate the cooperative effect in the H_2S pulse. Through this reaction pathway, tert-butylimido ligands have been desorbed as tert-butylamine and replaced by thiol groups. This terminates with the formation of bulk-like Mo (6 c.n.) in which Mo atoms covalently bond to the S atoms and O atoms at the interface. In addition, we found that the heterodeposition of MoS_2 from $\text{Mo}(\text{NMe}_2)_2(\text{N}^t\text{Bu})_2$ and H_2S leads to the formation of a buffer-layer, which might have important implications for the electronic and optical properties of the 2D material formed after subsequent homodeposition, similar to the buffer layer formed during epitaxial growth of graphene on SiC. Future work will be focused on the homodeposition of 2D- MoS_2 to form a complete picture of the ALD of 2D- MoS_2 and the implications of the buffer layer on the electronic structure of the formed 2D- MoS_2 material.

ASSOCIATED CONTENT

Supporting Information contains two figures. This material is available free of charge via the Internet at <http://>

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Funding Sources

This work has been funded by the European Research Council (ALDof2DTMDs, 648787).

ACKNOWLEDGMENT

This work was carried out on the Dutch national e-infrastructure with the support of SURF Cooperative.

ABBREVIATIONS

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