Strategies to facilitate the formation of free standing MoS2 nanolayers on SiO2 surface by atomic layer deposition: a DFT study

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Strategies to facilitate the formation of free standing MoS$_2$ nanolayers on SiO$_2$ surface by atomic layer deposition: A DFT study

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In this study, we employ density functional theory calculations to investigate the very initial formation of a buffer layer during atomic layer deposition of MoS$_2$ at the SiO$_2$ (001) surface. In our previous study, we described that the self-limiting atomic layer deposition (ALD) reactions using Mo(NMe$_2$)$_2$(N'tBu)$_2$ as precursor and H$_2$S as co-reagent terminate in the formation of a so-called building block on the SiO$_2$ (001) surface. This building block consists of Mo which shares bonds with the surface O of SiO$_2$ (001) at the bottom and terminal S at the top. Electronic band structure calculations indicate that the subsequently deposited buffer-layer that is composed of these building blocks has (opto)-electrical properties that are far from the ideal situation. Based on our studies, we propose alternative ALD chemistries which lead to the formation of a so-called underpinned building block. In this cluster, the Mo atoms are underpinned by S atoms, suppressing the formation of a buffer layer. This ultimately facilitates the formation of a free standing conformal 2D-MoS$_2$ nanolayer at the interface. Through the proposed chemistries, the opto-electrical properties of the deposited layers will be preserved. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5056213

The performance of (opto)-electronic devices depends heavily on the quality of its nanolayer components. The discovery of 2D-materials and their unique properties on the nanoscale have stimulated many studies with a focus on the implementation of 2D-materials into nanodevices. Traditionally, the (poly)crystalline 2D nanolayers have been isolated via top-down methods like mechanical exfoliation,$^1$ solution sonication,$^2$ and electrochemical exfoliation.$^3$ In spite of their success, these methods are of limited use due to low yield, small lateral dimensions, and difficulties in fabricating 3D structures.

Hence, one of the biggest challenges is the bottom-up large-scale growth of conformal nanolayers of 2D materials at the interface.$^4$ The conformal nanolayers should ideally be stoichiometric, free standing mono- to few-layer 2D materials with a uniform thickness along the interface. Growth of such conformal nanolayers should preferably occur at low temperatures to enable the integration with other semiconductor processing steps and materials. A number of vapor-phase techniques like chemical vapor deposition$^{5,6}$ and atomic layer deposition (ALD)$^7$–$^{10}$ have therefore been explored to grow mono- to a few-layers of 2D materials at the wafer-scale.

In our previous study,$^{11}$ we present a detailed description of the metal amide precursors and their advantage over alternative precursors. The by-products of the metal amide precursor are protonated ligands (dimethylamine and tert-butylamine) which are chemically inert by their strong C–H and N–H bonds and are therefore nonreactive and non-corrosive unlike the by-products of halide and carbon-monoxide precursors. Hence, we focus on the metal amide precursors. We used density functional theory (DFT) to describe the cyclic ALD reactions to form MoS$_2$ on a SiO$_2$ (001) surface.

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FIG. 1. Illustration of the formation of building block and underpinned building block from different metal precursors. (a) Adsorption of Mo\((\text{NMe}_2)_2(\text{N}^t\text{Bu})_2\) precursor at the terminal O at the SiO\(_2\) (001) surface. Two proton transfers from surface O to the ligands occur during adsorption of the metal precursor. This adsorption is exothermic by 1.79 eV. (b) shows the coordinated Mo and S atoms at the SiO\(_2\) surface after the H\(_2\)S pulse. The green rectangle represents the building block. (c) Adsorption of Mo\(_2\)(\text{BuAMD})\(_2\) at the terminal O site at the surface. This adsorption is exothermic by 0.70 eV. (d) shows the coordinated Mo and S atoms at the SiO\(_2\) (001) surface which compose an underpinned building block (green rectangle) at the end of H\(_2\)S pulse. In the underpinned building block, in contrast to the building block of (b), the Mo atom is underpinned by a S atom. This prevents the formation of direct chemical bond between Mo and surface O. (yellow = S, light blue = Mo, red = O, gray = Si, dark blue = N, dark gray = C, and white = H).

Atomic layer deposition of MoS\(_2\) is initiated by the exposure of metal precursor Mo\((\text{NMe}_2)_2(\text{N}^t\text{Bu})_2\) (bis(tert-butylimido)bis(dimethylamido)mothylenum) to the SiO\(_2\) surface [Fig. 1(a)] and then followed by the exposure of H\(_2\)S as co-reactant in the second pulse. The cyclic ALD reactions terminate in the formation of a buffer layer that consists of Mo atoms that share covalent bonds to O at the SiO\(_2\) surface and S at the top of the layer [Fig. 1(b)]. The formed cluster of Mo and S atoms at the surface composes a so-called “building block” at the SiO\(_2\) surface [green rectangle, Fig. 1(b)]. We expect that a similar sequence of ALD chemical reactions will take place when MoCl\(_5\) (molybdenum chloride), Mo\((\text{NMe}_2)_4\) (tetrakis(dimethylamido)molybdenum), Mo\((\text{CO})_6\) (molybdenum hexacarbonyl) precursors are used and that will lead to the formation of the same morphology at the interface. In several cycles of ALD, accordingly to the course of ALD reactions, the building blocks are formed and their coalescence leads to the formation of what will be called a buffer layer [Fig. 2(a)].

The electrical and optical properties of the buffer-layer resulting from the coalescence of the building blocks are most likely far from ideal. Hence, the formation of a buffer layer should be suppressed. Absence of a buffer layer means the direct formation of a free standing layer of 2D material stacked on the top of the substrate which is traditionally achieved using the exfoliation method. Here, through novel proposed chemistries, we will show the formation of an alternative building block, which we call “underpinned building block” [Fig. 1(d)]. In such underpinned building block, the Mo atom is underpinned by a S atom which is located in between Mo and O (green rectangle). In principle, the coalescence of the underpinned building blocks which have S “roots” could facilitate the direct formation of free standing MoS\(_2\) at the interface. In such a way, the formation of the buffer layer could be prevented or suppressed and a free standing MoS\(_2\) is directly formed on top of the surface. In addition, we study the electronic band structure of a layer of MoS\(_2\) at the interface using DFT calculations and we will show how the (opto)-electronic properties of MoS\(_2\) at the interface are sensitive to the presence of these S roots at the interface between Mo and O.
The current DFT calculations show that the traditional ALD chemical reactions lead to the formation of building blocks that coalesce to form a buffer layer of amorphous MoS$_2$ at the top of the SiO$_2$ surface rather than free standing MoS$_2$ layers. The main reason is the large mismatch between the structure of the formed MoS$_2$ after the initial cycles of ALD and the crystalline SiO$_2$ surface. To show this discrepancy, we count the number of Mo and Si present in the interface and ignore the number of O and S. The crystalline SiO$_2$ (001) surface contains 12 Si atoms per layer in our slab. The chemical ALD reactions of Mo(NMe$_2$)$_2$(NtBu)$_2$/H$_2$S on SiO$_2$(001) gives rise to the formation of coordinated Mo and S at the SiO$_2$ surface. In this situation, Mo has coordination number (c.n.) of 6 while S has either 1 c.n. or 2 c.n. (excluding H). The ALD reactions give rise to the optimized formation of 9 Mo on the slab [Fig. 2(a)], while in the ideal situation, 28 Mo should be situated in this surface area [see Fig. 2(c)]. These numbers are obtained according to the course of ALD reactions which terminated to 6 coordinated Mo at the interface. When higher numbers of Mo in the surface area are considered, low coordinated Mo is formed at the interface. Such morphology at the interface is not fully optimized and does not follow the course of ALD reactions.

The DFT calculations show that the deposited film from Mo(NMe$_2$)$_2$(NtBu)$_2$/H$_2$S has an amorphous structure. To describe the morphology of the thin-film at the interface, only two layers have been considered. This amorphous structure can either spread along the z-direction through different number of MoS$_2$ layers [Fig. 2(b)] or can be transformed into free standing few layers of MoS$_2$ at the SiO$_2$ interface [Fig. 2(c)]. The crystalline free standing layers of MoS$_2$ could be experimentally formed after annealing of deposited amorphous layers in a sulphur containing atmosphere. In this practice, Mo and S atoms would diffuse inter- and intra-layer to form the crystalline film. Ideally, the thickness of the deposited thin-film should be as low as a mono-layer (ML) of MoS$_2$ and the deposited thin-film should readily obtain the structure of the free standing layered MoS$_2$ at a low temperature as in Fig. 2(c). These criteria are more compatible with the direct fabrication of electronic devices. For this purpose, if in the initial stage of growth, a higher number of S atoms could possibly be situated at the SiO$_2$ surface without reducing the SiO$_2$ surface or without replacing surface O with S, then higher number of Mo can be deposited in the same area at the surface, facilitating the direct formation of free-standing MoS$_2$. Strategies to situate S in between the SiO$_2$ surface and the Mo will be discussed later in this paper. Here, we first focus on the consequence of the absence of these S atoms in the deposited MoS$_2$ layers (S vacancies) on its electronic band structure.

The electrical and optical properties of the thin film layer depend on the crystallinity and stoichiometry of the deposited thin film layer. In the following discussion, we describe the electronic structure of a pristine mono-layer of MoS$_2$ and continue by the creation of S vacancies in a free-standing mono-layer of MoS$_2$. This is followed by the creation of S vacancies in a mono-layer of MoS$_2$ that interact with the SiO$_2$, ending in a situation that represents the buffer layer. In order to simulate the consequence of S deficiency on the opto-electronic properties of MoS$_2$, deposited by
ALD, two scenarios will be built. The first case is constructed by random removal of S from a pristine layer of MoS$_2$, and the second case is constructed by random removal of S from the interface.

First, the electronic band structure of free-standing bulk MoS$_2$ and mono-layer MoS$_2$ has been calculated. Bulk MoS$_2$ showed an indirect bandgap of 0.88 eV while mono-layer MoS$_2$ showed a direct bandgap of 1.75 eV which is in good agreement with reported values from both experimental and theoretical work.$^{12-14}$ In addition, the electronic structure of $3 \times 3$ and $5 \times 5$ supercell (SC) of mono-layer MoS$_2$ has been calculated. The same direct band of 1.75 eV at K point is obtained in all band structure calculations (supplementary material Fig. 1).

As indicated in insets of (supplementary material Fig. 2), S atoms are randomly removed (green atoms). The creation of S vacancies in the $3 \times 3$ SC leads to the formation of energy states in the bandgap of the free standing MoS$_2$ layer. The introduction of more S vacancies gives rise to the formation of even more energy states in the bandgap. This can be observed from supplementary material Figs. 2(b)–2(d).

In the next step, we studied the effective band structure (EBS) of a free standing monolayer of MoS$_2$ on the O-terminated SiO$_2$ (001) surface as a function of S vacancies at the interface. The results are depicted in Fig. 3. As site projected band structures are unavailable in this implementation, some noise is present in the figure due to the states of the substrate. A simple inspection of the bandgap reveals a direct bandgap of 1.50 eV [Fig. 3(a)]. On top of SiO$_2$, the MoS$_2$ remains semiconducting while the bandgap reduces slightly. This is similar to the calculation of the single layer of MoS$_2$ on $\alpha$-Al$_2$O$_3$ substrate reported by Singh et al.$^{15}$ In addition, the expansion of the current structure to $2 \times 2$ SC also shows the same direct bandgap of 1.50 eV (supplementary material Fig. 3).

The (opto)-electronic properties of deposited MoS$_2$ at the interface are sensitive to S vacancies at the interface. Here, through the EBS calculations, we describe the consequence of absence of S in between Mo and O on the electronic structure of MoS$_2$ (as shown in the formation of the buffer layer). S atoms have been removed randomly one by one from the interface (green atoms). Figure 3(b) shows the removal of the first S. Once the first S is taken away, a surface O has been transferred from the surface to the MoS$_2$ layer during geometry optimization. The removal of the first S leads to the shift of direct bandgap downward, but it still has the value of 1.55 eV. The removal of second S is depicted in Fig. 3(c). The removal of second S leads to the formation of a bond between O and Mo,
but the surface O did not entirely transfer to the MoS$_2$ monolayer. The band structure shows that some energy states appear in bandgap around 0.05 eV which deteriorate the semiconductor behavior of MoS$_2$. The removal of third S leads is depicted in Fig. 3(d). The EBS does not show the characteristic primitive cell band structure of mono-layer MoS$_2$ anymore and many intermediate states appeared in bandgap. This may not be considered a perturbed system of a MoS$_2$ layer anymore.

From the simulations presented above, it becomes immediately clear that the formation of a buffer layer is undesired for the electrical properties. In the following discussion, we describe the chemistry that could be used to place S atoms at the interface to prevent Mo–O bonding and to facilitate formation of free standing MoS$_2$. We suggest two possible chemistries. First, the usage of a heteroleptic precursor like MoS$_2$(BuAMD)$_2$ (AMD = acetamidinato) or MoS$_2$Cl$_2$. These heteroleptic precursors carry a strong Mo–S bond to the surface, and their remaining ligands can be replaced by S atoms through ligand exchange. Second, the usage of diethyl sulphide (C$_2$H$_5$)$_2$S, diethyl disulphide (C$_2$H$_5$)$_2$S$_2$, diethyl trisulphide (C$_2$H$_5$)$_2$S$_3$, dimethyl tetrasulphide (CH$_3$)$_2$S$_4$, and dimethyl pentasulphide (CH$_3$)$_2$S$_5$ as sulphur co-reagent is considered. These sulphur co-reagents could be used in a separate pulse in the ALD cycles to deposit a seed layer of S atoms at the very initial of ALD growth on the SiO$_2$ surface and could bind to the SiO$_2$ surface to form a sulfur-rich seed layer for precursor adsorption. This could prevent Mo–O bond formation.

Recently, the ALD precursor MoO$_2$(BuAMD)$_2$ was used with O$_2$/H$_2$O as co-reagent to deposit MoO$_3$. The deposited thin-film formed the layered structure of MoO$_3$ after annealing at temperature of 500 °C. In this heteroleptic precursor, Mo chemically bonds with N of acetamidinato-ligands and strongly bonds to O. In this type of precursor, the fragment of the precursor is what should be deposited as a thin film. Here, for example, MoO$_2$ is a fragment of MoO$_3$(BuAMD)$_2$ which used to deposit MoO$_3$.

The MoS$_2$(BuAMD)$_2$ precursor has not been synthesized yet, but we expect that this precursor could be synthesized like MoO$_2$(BuAMD)$_2$. The reaction energy of ALD reactions of MoS$_2$(BuAMD)$_2$/H$_2$S on the SiO$_2$ (0001) is calculated. The ALD reactions proceed through many intermediate reactions which may be exothermic or endothermic (see supplementary material Figs. 4–6 and Table I). In this contribution, we do not aim to create deep understanding of these chemical reactions. Here, we calculate the reaction energy of precursor absorption, protonation of the ligands, ligand desorption, and ligand exchange. The ALD reactions will ultimately result in the formation of a building block regardless thermal or plasma ALD is used.

The first step of adsorption has been depicted in Fig. 1(c). Unlike Mo(NMe$_2$)$_2$(N$^t$Bu)$_2$, the Mo atom in MoS$_2$(BuAMD)$_2$ has two strong bonds with S. Therefore, in the initial deposition of MoS$_2$, the already present Mo–S bond could prevent the formation of a direct bond between the surface O and Mo, and S atoms could be located beneath Mo. This reduces the possibility of Mo–O bond formations. Therefore, the ultimately deposited building block from MoS$_2$(BuAMD)$_2$/H$_2$S has an underpinned building block structure [Fig. 1(d)] and the coalescence of the underpinned building blocks from MoS$_2$(BuAMD)$_2$/H$_2$S should be easier than the coalescence of building blocks from Mo(NMe$_2$)$_2$(N$^t$Bu)$_2$/H$_2$S. The repetition of cyclical ALD reactions directly gives rise to the formation of a free standing MoS$_2$ at the SiO$_2$ (001) surface in this case.

In the second proposed chemistry, the sulphur co-reagents are introduced to the reactive OH and O sites at the SiO$_2$ (001) surface to see whether these compounds can form a sulfur rich seed layer. As a general trend, none of sulphur co-reagent chemically bond to the terminal OH sites at the surface (see supplementary material Figs. 7–15 and Table II). In addition, dissociative adsorption of sulphur co-reagent to the adsorbed precursor fragment and ethane was chemically unfavorable in the case of diethyl sulphide and diethyl disulphide. Hence, we did not calculate the dissociative adsorption of other sulphur co-reagents. By contrast, the introduction of sulphur co-reagents to the terminal O sites at the SiO$_2$ surface gives rise to the chemical adsorption of the sulfur containing co-reagent. The adsorption of diethyl sulphide (C$_2$H$_5$)$_2$S, diethyl disulphide (C$_2$H$_5$)$_2$S$_2$, diethyl trisulphide (C$_2$H$_5$)$_2$S$_3$, dimethyl tetrasulphide (CH$_3$)$_2$S$_4$, and dimethyl pentasulphide (CH$_3$)$_2$S$_5$ are exothermic by 2.20 eV, 2.42 eV, 2.37 eV, 1.75 eV, and 2.62 eV, respectively. Associative desorption of CH$_4$ and C$_2$H$_6$ from adsorbed sulphur co-reagent is mainly unfavorable. Therefore, the sulphur co-reagents strongly adsorb on the surface and the adsorbed co-reagent is the energetically most favorable configuration that could deliver S atoms to the SiO$_2$ surface. Indeed, this is in excellent agreement with the experimental
study\textsuperscript{17} of the pretreatment of the SiO\textsubscript{2} surface with diethyl sulphide. The pretreatment improves the stoichiometry and the grain size of the deposited MoS\textsubscript{2} thin film and reduces the amount of Mo–O bonds.

The deposited S atoms of the co-reagent in the very initial stage of ALD growth could be accounted as adsorption sites for a typical metal precursor, e.g., Mo(NMe\textsubscript{2})\textsubscript{4}.\textsuperscript{8} The chemical adsorption of Mo(NMe\textsubscript{2})\textsubscript{4} at S sites is depicted in Fig. 4. The chemical adsorption of Mo(NMe\textsubscript{2})\textsubscript{4} at S of diethyl disulphide, diethyl trisulphide, dimethyl tetrasulphide, and dimethyl pentasulphide is exothermic by 0.69 eV, 0.13 eV, 0.50, and 0.15 eV. By contrast, Mo(NMe\textsubscript{2})\textsubscript{4} does not chemically bond to S of diethyl sulphide due to steric effects between the ethyl ligand and dimethylamido ligand. In addition, the introduction of Mo(NMe\textsubscript{2})\textsubscript{2}(\textit{Nt}Bu)\textsubscript{2} to S of the adsorbed sulphur co-reagents does not lead to the chemical bond between Mo and S (supplementary material Fig. 16). This implies that chemical reactivity of Mo(NMe\textsubscript{2})\textsubscript{2}(\textit{Nt}Bu)\textsubscript{2} toward S sites of the adsorbed sulphur co-reagent is less than Mo(NMe\textsubscript{2})\textsubscript{4}.

In summary, DFT calculations show that the self-limiting ALD reactions using typical precursors such as Mo(NMe\textsubscript{2})\textsubscript{2}(\textit{Nt}Bu)\textsubscript{2}, MoCl\textsubscript{5}, Mo(NMe\textsubscript{2})\textsubscript{4}, and Mo(CO)\textsubscript{6} and H\textsubscript{2}S as the co-reagent result in the formation of a building block on the surface that consists of Mo which shares bonds with the surface O of the SiO\textsubscript{2} (001) surface at the bottom and S at the top. The coalescences of the building blocks gives rise to the formation of a buffer-layer which is far from the ideal situation.

![FIG. 4. Chemical adsorption of Mo(NMe\textsubscript{2})\textsubscript{4} at the terminal S sites, deposited from sulphur co-reagents pulse. Chemical adsorption of Mo(NMe\textsubscript{2})\textsubscript{4} gives rise to the bond dissociation between S atoms. The insets show the initial configuration. (a) The chemical adsorption at S of diethyl disulphide is exothermic by 0.69 eV. (b) The chemical adsorption at S of diethyl trisulphide is exothermic by 0.13 eV. (c) The chemical adsorption at S of dimethyl tetrasulphide is exothermic by 0.50 eV. (d) The chemical adsorption at S of dimethyl pentasulphide is exothermic by 0.15 eV.](image-url)
of free standing MoS₂ at the interface. Electronic structure calculations show that the S vacancies at the interface have a detrimental effect on the electronic properties of the deposited layer. The semiconducting behavior of the deposited MoS₂ can be preserved when S atoms are situated at the surface of the SiO₂ (001) substrate (underpinned building block) in the very first stages of ALD. Based on reaction energy calculations, we propose two possible chemistries to deposit the underpinned building blocks at the interface by ALD. First, the usage of a heteroleptic precursor, in which the fragment of the molecule is what should be deposited [e.g., MoS₂( t-BuAMD)₂ or MoS₂Cl₂]. Second, the usage of a sulphur co-reagent such as diethyl disulphide or dimethyl tetrasulphide in a separate pulse to deposit a seed layer of S at the very initial stage of growth. The proposed chemistries prevent the formation of a direction bond between Mo and surface O and facilitate the coalescence of deposited underpinned building blocks to form a free standing MoS₂ at the interface.

Geometry optimization, reaction energies, and electronic band structure of the system are performed by self-consistent DFT calculations in the generalized gradient approximation (GGA) approximation within a 3D periodic model, using VASP. In these calculations, the electronic energies are approximated using the projector augmented wave (PAW) description of atomic cores and the functional of Perdew, Burke, and Ernzerhof (PBE). The plane wave cutoff energy is set to 600 eV. For Mo atoms 4d⁵5s¹, S atoms 3s²3p⁴, N atoms 2s²2p³, C atoms 2s²2p², O atoms 2s²2p², and Si atoms 3s²3p², electrons are included as valence electrons. The self-consistent steps are converged to an energy difference of at least 10⁻⁵ 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 kinetics, all calculations are spin-polarized.

To study the formation of MoS₂ as a buffer layer on the SiO₂(001) surface, five layers of SiO₂ is considered as a slab. Converged values of the surface energies of the SiO₂(001) surface show that five layers of SiO₂ 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 × 8 × 8 and 4 × 4 × 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 × 2 × 1. Each layer of the slab has 12 Si atoms and is considered as a mono-layer (ML). The H-coverage is calculated based on the number of H-atom at the SiO₂ surface divided by number of Si in a ML.

To build the interface between the MoS₂ surface and the SiO₂ surface, the unit cell of 2H-MoS₂ with space group of P6₃/mmc and the unit cell of SiO₂ (α-quartz) with space group of P₃₋₁m is initially optimized by 12 × 12 × 12 grid size. The bond length of Si–O is 1.62 Å, the bond length of Mo–S is 2.40 Å, and the interlayer spacing of 2H-MoS₂ is 3.00 Å. Then, we create a cell of MoS₂ monolayer with the size of 3 × 3 along (001) surface and a SiO₂ cell with the size of 2 × 2 along (001) surface. The two cells are not entirely compatible. Therefore, in order to achieve matching of the MoS₂ and SiO₂ cell, the lattice parameter of the SiO₂ cell was reduced by 3.5% to fit the theoretical value of the MoS₂ cell. Such an adjustment results in an artificial destabilization of the SiO₂ surface and shifts of the SiO₂ surface and bulk bands to higher energies, but here we focus on the electronic structure of MoS₂. In addition, a 2 × 2 supercell (SC) of the formed interface has been considered. The effective band structure (EBS) calculation shows the similar electronic band structure (see supplementary material Fig. 3).

The MoS₂ cell contains 3 layers of Mo and S which compose a monolayer of MoS₂. Similarly, the SiO₂ cell contains 11 layers of Si and O which the top and bottom of cell is terminated with surface O. The mono-layer of MoS₂ stacked on top of the SiO₂(001) surface along the z-direction. Periodicity in all direction is ensured, and a vacuum region of 5 Å is imposed on the top of the MoS₂ surface and on the bottom of the SiO₂ surface. The initial distance of 2.0 Å is considered between two surfaces which are adjusted between the closest atoms in the MoS₂ surface and the SiO₂ surface, but this value has been reduced to 1.53 Å during optimization and leads to the formation of bond between O and S.

The unfolding has been performed using the BandUP code. The geometry of the interface was optimized using K-point sampling of 4 × 4 × 4, and the charge density was subsequently recalculated
with a single point calculation using a dense K-point sampling \((7 \times 7 \times 1)\). To plot the band structure, 50 k-points are considered between the supplied points \((\Gamma, M, \text{and} K)\).

The inclusion of van der Waals functional \((\text{optPBE-vdW})\), developed by Michaelides and co-workers,\(^{24,25}\) did not show a significant change on EBS. The interaction between surface O and S at the interface has the characteristic of a covalent bond and therefore van der Waals interaction has not been considered for the rest of calculations \(\text{(see supplementary material Fig 3).}\)

See supplementary material for the further details provided in the entire paper.

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