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Surface Defect Engineering of MoS₂ for Atomic Layer Deposition of TiO₂ Films

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Abstract: In this manuscript we combine experimental and computational approaches to study the Atomic Layer Deposition (ALD) of dielectrics on MoS₂ surfaces for a very common class of ALD precursors, the alkylamines. More specifically we study the thermal ALD of TiO₂ from TDMAT and H₂O. Depositions on as-produced Chemical Vapor Deposition MoS₂ flakes result in discontinuous films. Surface treatment with mercaptoethanol (ME) do not improve the surface coverage and DFT calculations show that ME reacts very weakly with the MoS₂ surface. However, creation of sulfur vacancies on the MoS₂ surface using Ar ion beam irradiation results in much improved surface coverage for films with nominal thickness 6 nm, and the calculations show that TDMAT reacts moderately with either single or extended sulfur vacancies. ME also reacts with the vacancies, and defect-rich surfaces treated with ME provide an equally good surface for the nucleation of ALD TiO₂ films. The computational studies though reveal that the creation of surface vacancies results in the introduction of gap states that may deteriorate the electronic properties of the stack. Treatment with ME results in the complete removal of the gap states originating from the most commonly found single vacancies and reduces substantially the density of states for double and line vacancies. As a result, we provide a pathway for the deposition of high quality ALD dielectrics on the MoS₂ surfaces, which is required for the successful integration of these 2D materials in functional devices.

INTRODUCTION

Monolayer molybdenum disulfide (MoS₂) is a two-dimensional (2D) semiconductor material that primarily exists in a hexagonal structure (2H-MoS₂). Monolayer 2H-MoS₂ possesses a direct band gap of ~1.8 eV and is therefore of interest for electronic, optoelectronic, and sensing applications.^{1,2} Recently, chemical vapor deposition (CVD) methods have been developed to grow high quality, large-area single crystal MoS₂ monolayers.³⁻⁷ If these MoS₂ monolayers are to be used in a device such as a field-effect transistor, they need to be integrated with a high quality dielectric material. Atomic layer deposition (ALD) has been used extensively to

deposit high-k dielectric films on mainstream semiconductors because of the high film quality, purity and the ability to coat non-planar geometries. For ALD of metal oxide films, a hydrophilic surface is required.⁸ This is usually accomplished by preparing the starting surface with an -OH termination which is fairly straightforward for surfaces covered with an oxide layer. The MoS₂ surface, however, is inert and hydrophobic. A prime example of ALD of metal oxides on inert, hydrophobic surfaces is the hydrogen-terminated Si (Si-H) surface that has been studied extensively. For Si-H surfaces in general it is known that film formation occurs on defect sites. The Si-H surface is unstable at normal processing

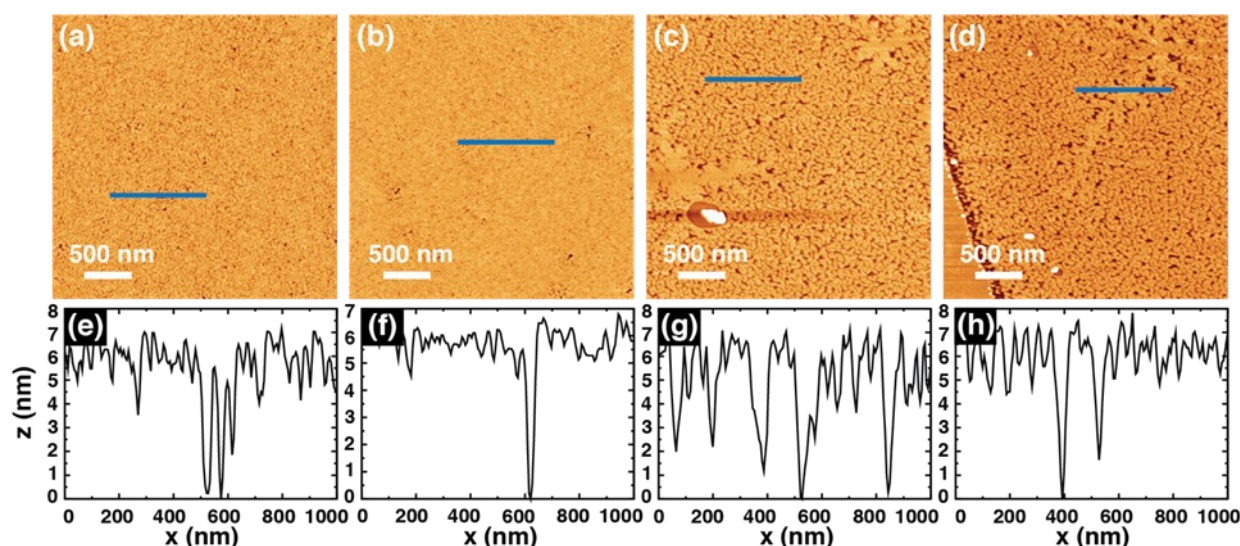


Figure 1. AFM images of 6 nm TiO_2 deposited on (a,b) untreated MoS_2 and (c,d) MoS_2 treated with mercaptoethanol. Blue bars mark the location of line profiles shown below each image in (e,f) for untreated MoS_2 and (g,h) for treated MoS_2 .

temperatures leading to the progressive increase of the defect density and eventually the formation of continuous films after what is known as an incubation period.⁹ Like Si-H, the MoS_2 surface is inert and hydrophobic, but unlike Si-H, it is stable at normal processing temperatures and as a result not an ideal starting surface for the ALD of metal oxide films. Typical MoS_2 surfaces contain up to ~10% sulfur vacancies which are more reactive than the pristine surface and may serve as nucleation sites for ALD films.¹⁰ However, at this concentration the defects are not sufficient to produce continuous coverage even for films several nanometers in thickness. As a result, the creation of higher defect density or the introduction of an anchor species on the surface is required to seed growth. Such a molecule should have two different end groups: one that would interact with the -S surface termination and -OH termination on the opposite side to seed film growth. There are examples where one of these approaches have been used to achieve uniform, pinhole-free films on MoS_2 .^{11–22}

In this work, we investigate the effect of sulfur vacancies on the surface coverage obtained for a typical ALD process by using Ar ion sputtering to control their density. While defect creation may increase the reactivity of the MoS_2 surface, Density functional theory (DFT) calculations of the electronic band structure show that such vacancies introduce localized states into the band gap. We therefore investigate the effectiveness mercaptoethanol (ME) as a seed for the ALD of TiO_2 both on as-received and argon ion-treated CVD MoS_2 surfaces. Mercaptoethanol ($\text{HOCH}_2\text{CH}_2\text{SH}$) is a short thiol with an -SH group at the tail and is hydroxyl (-OH) terminated on its other end, and thus meets the anchor molecule requirement stated before. Thiols are known to interact with the naturally occurring vacancies and may be used to heal the vacancies and restore the electronic properties of the MoS_2 surface.^{20,23–28,21,29–34} The experimental work is complemented by calculations of the energetics of thiol and ALD precursor

adsorption on pristine and vacancy-containing MoS_2 surfaces using density functional theory. This combined approach provides significant insight into the mechanism of ALD film growth on MoS_2 .

RESULTS

Atomic Layer Deposition of TiO_2 on MoS_2

Deposition of TiO_2 films on untreated MoS_2 monolayers results in non-continuous films that contain many pinholes. As an example, Figure 1a,b shows AFM images of 6 nm TiO_2 deposited on MoS_2 at 100°C . AFM line profiles measure the depth of the pinholes as ~6 nm. MoS_2 surfaces are hydrophobic so it is not surprising that the ALD process fails to provide continuous coverage. This also demonstrates the need to alter the surface energy so as to promote film nucleation. ME is a thiol with an -OH group on the opposite end and we hypothesize that the presence of this group on the surface would provide more film nucleation sites. However, depositions of 6 nm films on ME treated surfaces (Figure 1c,d) result in films that contain wider pinholes and on average show decreased surface coverage than films on the untreated surfaces.

We use DFT calculation to study the interaction of ME with various MoS_2 surfaces (Figure S1, Table S1) and we find that the ME interacts only weakly with pristine surfaces but more strongly with sulfur vacancies. Clearly the results in Figure 1c,d show that the natural abundance of defects on the MoS_2 surface is not high enough to result in continuous film coverage. So as to create a higher concentration of reactive defect sites, we sputter the MoS_2 monolayers with argon ions.

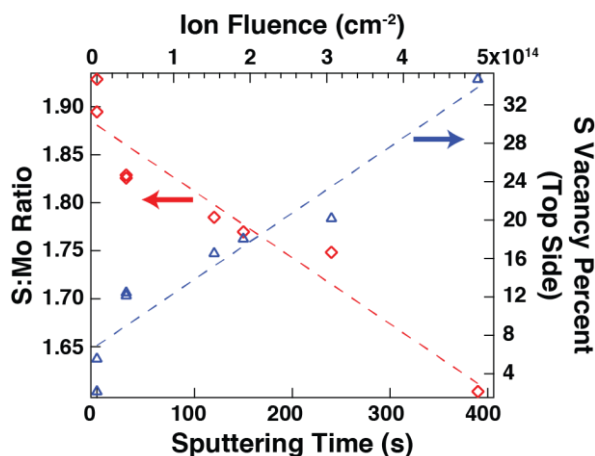


Figure 2. The left axis (red line) plots the sulfur:molybdenum ratio of MoS₂ as a function of sputter time/ion fluence as calculated from XPS peak fitting. The right axis (blue line) plots the calculated sulfur vacancy percentage on the top side as a function of sputter time/ion fluence. Multiple data points at 0 s and 30 s correspond to measurements taken on two separate samples.

Analysis of the XPS results show that the as-grown CVD MoS₂ surface contains ~5% vacancy sites, which includes possible defects present on both sides of the monolayer. The evolution of the surface defect density as a function of sputter time and ion fluence is shown in Figure 2. Sputtering for 390 s (corresponding to an ion fluence of $F = 4.97 \times 10^{14} \text{ cm}^{-2}$) generates up to 35% sulfur vacancies on the top side. The shortest sputter duration, 30 s ($F = 3.83 \times 10^{13} \text{ cm}^{-2}$), generates ~10% sulfur vacancies. It is expected that the vacancies generated by sputtering are on the top side of the MoS₂ surface only as a consequence of the sample geometry.

Ion bombardment is a highly invasive surface treatment, so it is important to consider its effect on the surface structure. Argon plasma has been shown to induce a phase change in MoS₂, and the change from the 2H phase to the 1T phase is detectable with XPS analysis.³⁵ High resolution XP spectra of the Mo 3d and S 2p regions (Figure 3) taken before and after ion sputtering show little change in peak shape. This confirms that the treatment did not induce phase changes or destroy the MoS₂ layer, but preferentially creates sulfur vacancies on an otherwise intact 2H-MoS₂ surface.

The sputtered MoS₂ samples (up to 390s - ~35% S vacancies) are treated with mercaptoethanol vapor before subsequent ALD of 6 nm TiO₂. As a control, we also perform ALD on sputtered samples with no thiol treatment. AFM characterization of the surface morphology of TiO₂ films on sputtered, ME-treated MoS₂ samples reveals films that are uniform and pinhole-free (Figure 4a-c). TiO₂ films on the control MoS₂ samples are similarly uniform and free of pinholes (Figure 4g-i). This suggests that the increased concentration of sulfur vacancies alone, as compared to as-grown CVD MoS₂, is sufficient to promote smooth,

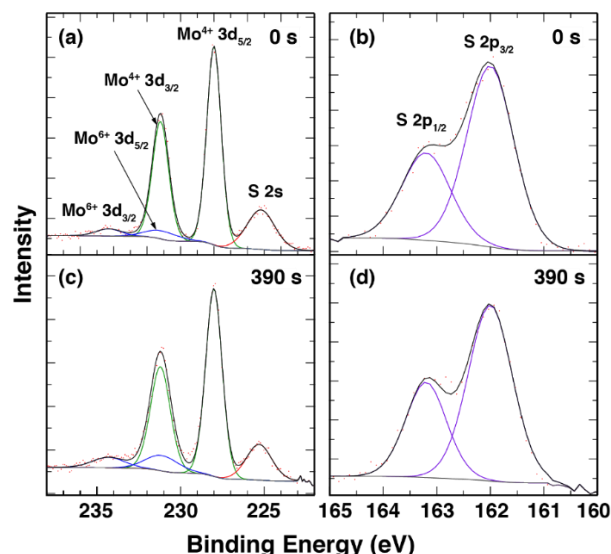


Figure 3. X-ray photoelectron spectra of the (a) Mo 3d region (no sputtering) and (b) S 2p region (no sputtering), and the (c) Mo 3d region (390s sputtering) and (d) S 2p region (390s sputtering).

conformal, and coalesced ALD film growth. Both sets of samples exhibit dendritic structures on the surface that are ~1 nm in height. Similar features have been observed in thermally oxidized MoS₂, and it is possible that these dendrites are formed by oxidation of the defective MoS₂ layer.³⁶

O₂, H₂O, and TDMAT Adsorption on Bare MoS₂ and S Vacancies

Motivated by the observation of uniform film growth on the untreated 10-35% vacancy-containing MoS₂ (Figure 4g-i), we calculate the adsorption energy of O₂, H₂O, and TDMAT molecules on the pristine and single S vacancy site. We consider O₂ and H₂O molecules as possible seed molecules for TiO₂ film growth, as they are abundant in air and may react with TDMAT to form TiO₂.^{37,38} It has been reported in the literature that O₂ and H₂O do not bind strongly with the pristine MoS₂ surface.^{39,40} The final geometry and adsorption energy for these molecules on the S vacancy are shown in Figure 5. Calculation parameters and simulation details can be found in the “Computational Methods” section. The adsorption energy of TDMAT on MoS₂ is calculated in a 6×6×1 supercell to avoid interactions between the relatively large TDMAT molecule and its periodic images. In agreement with previous works, we find that O₂ and H₂O adsorb weakly above the S vacancy.^{41,42} TDMAT binds most strongly of all molecules considered here, with adsorption energy of -0.43 eV. On the pristine MoS₂ surface, TDMAT adsorbs with an energy of -0.23 eV. Similar calculations for the interaction of ME with the MoS₂ surfaces are shown in the supporting information.

Adsorption on Extended Defects

Because of the high concentration of defects on our sputtered MoS₂ surfaces, it is likely that extended defects are present. Cluster expansion is used to generate structures with the desired sulfur vacancy concentration (0-40%) and identify the most favorable arrangement of the vacancies (Figure S2). The cluster expansion calculations reveal that, in addition to single sulfur vacancies, extended line defects of missing sulfur atoms are favorable at these defect concentrations (Figure S3). Thus, we investigate the adsorption of the above-mentioned species and ME on both an extended line defect and a simpler double sulfur (S₂) vacancy. ME physisorbs above the S₂ vacancy with an energy of -0.25 eV which is similar to the adsorption energy on a single S vacancy. Once trapped in the physisorption well, there is a very small thermal barrier (0.09 eV) to transition to the chemisorbed state where it is strongly

bound ($E_{ads} = -2.43$ eV). The energetics of this process are shown in Figure 6. In the resulting geometry, the S-H bond is broken, and the thiol chain passivates one sulfur vacancy site while the H atom bonds in the neighboring site. The thiol chain binds with energy -1.39 eV and remains chemisorbed in the vacancy after 1 ps of AIMD simulations at 600 K, indicating that this system is dynamically stable. These results show similarities with the single S vacancy, but the energy barrier for the ME molecule to bind inside the vacancy is reduced significantly. The adsorption energetics of O₂, H₂O, and TDMAT on the S₂ vacancy are similar to the single vacancy case. In contrast, the physisorption of these molecules on extended line vacancies is stronger than with either the single S or S₂ vacancies. The adsorption energies are compiled in Table 1.

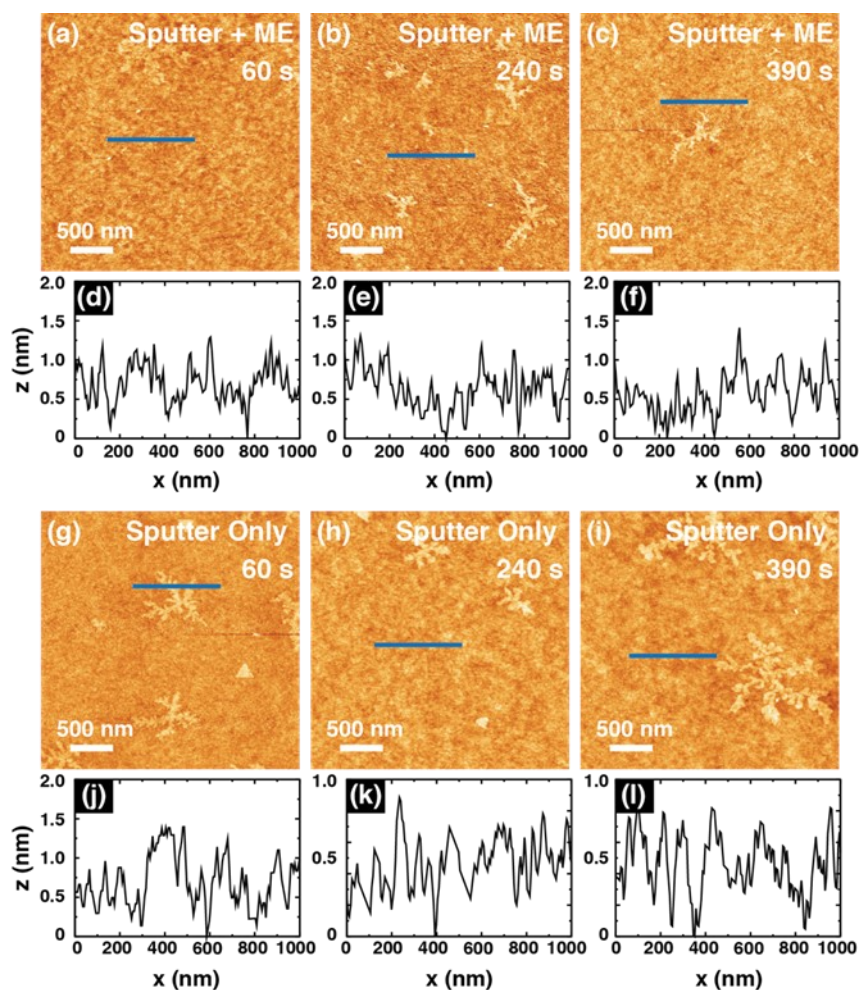


Figure 4. AFM images of 6 nm TiO₂ deposited on ME-treated MoS₂ that was sputtered for (a) 60 s, (b), 240 s, and (c) 390 s. Line profiles marked by the blue bars are shown for sputter times of (d) 60 s, (e), 240 s, and (f) 390 s. Also shown are AFM images of 6 nm TiO₂ deposited on untreated MoS₂ that was sputtered for (g) 60 s, (h) 240 s, and (i) 390 s with corresponding line profiles shown in (j), (k), and (l).

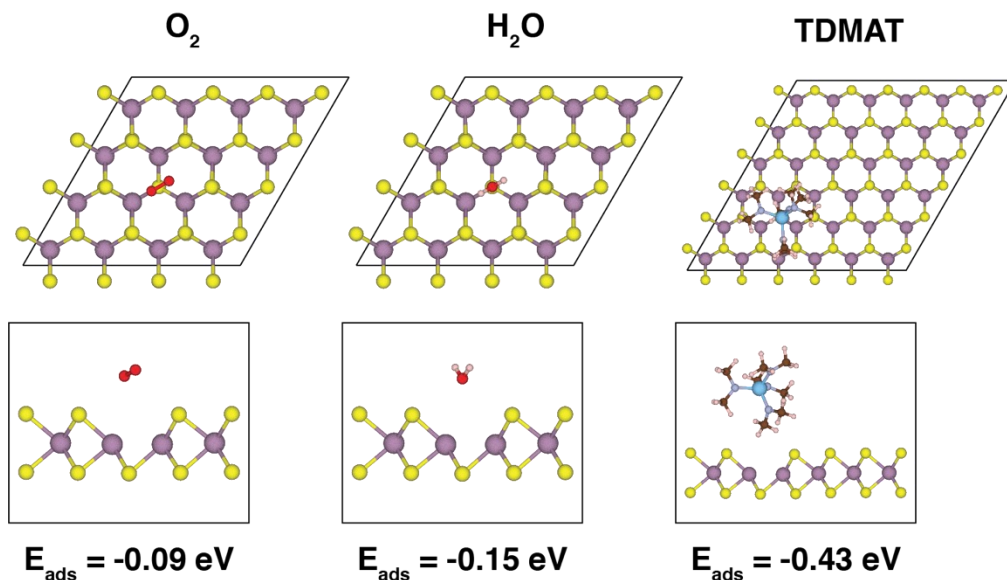


Figure 5. Adsorption geometry and energy of O₂, H₂O, and TDMAT on a single S vacancy. The atoms shown in the figure are: Mo (purple), S (yellow), O (red), C (brown), H (white), N (pale blue), and Ti (bright blue).

We further investigate the chemisorption and dissociation of O₂ and H₂O on vacancy defects, as O₂ dissociation on the single S vacancy has previously been found to be favorable.^{43,44} The O₂ molecule may chemisorb in the S₂ vacancy by overcoming an energy barrier of ~0.1 eV and the resulting adsorption energy is $E_{ads} = -2.30$ eV (see Figure S4e). Furthermore, dissociation of the O₂ molecule in the S₂ vacancy is energetically the most favorable and results in $E_{ads} = -7.94$ eV. The resulting configuration in this case is that each oxygen atom occupies neighboring S vacancy sites (Figure S4f).

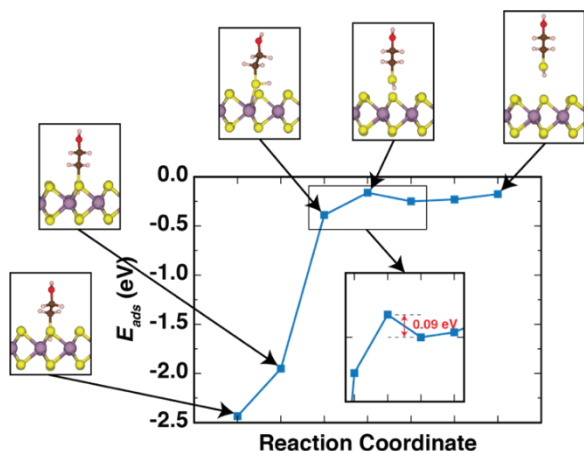


Figure 6. Energy barrier calculations of the ME molecule in a sulfur double vacancy. The inset shows the barrier measured at ~0.09 eV. The atoms shown in the figure are: Mo (purple), S (yellow), O (red), C (brown), and H (white)

Since previous works have shown that the O₂ molecule may dissociate on the S vacancy leaving one oxygen atom adsorbed on the surface,^{43,44} we calculate the energy of similar configurations on both single S (Figure S4g) and double S₂ (Figure S4h) vacancies. These “functionalized” cases result in $E_{ads} = -4.65$ eV and $E_{ads} = -4.12$ eV for S and S₂ vacancies, respectively. Unlike the O₂ molecule, the H₂O molecule does not chemisorb in the double vacancy but remains physisorbed on the surface.

Since the chemisorption of oxygen in extended sulfur vacancies is likely, we investigate further the adsorption of ME and TDMAT molecules on these oxygen-containing MoS₂ surfaces (Table 2). First, we consider the case of the O₂ molecule chemisorbed in the S₂ vacancy (Figure S4e). ME interaction with this system is weak, with $E_{ads} = -0.15$ eV, but TDMAT can adsorb with $E_{ads} = -0.39$ eV. Next, we consider adsorption on the dissociated O₂ molecule in the S₂ vacancy. Here, ME may adsorb with $E_{ads} = -0.28$ eV, which is comparable to the adsorption energy of ME on an unpassivated single S vacancy. TDMAT adsorbs with $E_{ads} = -0.45$ eV, which is again comparable to its interaction with a single S vacancy. We can conclude that oxygen chemisorption on the defective MoS₂ surface has minor effects (either none or slightly lowering the adsorption energy) on the adsorption of ME and TDMAT. Similar binding trends are calculated for extended line vacancy defects (Table 1).

Electronic Structure

In order to investigate the utility of defective and functionalized MoS₂ for electronic devices, we calculate the band structures and density of states of pristine, defective, and thiol-functionalized MoS₂ monolayers using DFT. The band

Table 1. Adsorption energies of mercaptoethanol, TDMAT, O₂, and H₂O on MoS₂ surfaces. The surfaces considered are pristine MoS₂ (Figure S4a), MoS₂ with a single S vacancy (Figure S4b), MoS₂ with a double S vacancy (S₂ vacancy, Figure S4c), and MoS₂ with a line vacancy (Figure S4d).

Surface	Molecule	Adsorption Energy on Site (eV)			
Pristine MoS ₂ (Figure S4a)		Top S	Top Mo	Bridge	Hollow
	Mercaptoethanol	-0.15	-0.18	-0.14	-0.17
	TDMAT	-0.22	-	-	-
	O ₂	-0.02	-	-	-
	H ₂ O	-0.04	-	-	-
MoS ₂ Single S Vacancy (Figure S4b)		Top S Vacancy (Physisorbed)	In S Vacancy (Chemisorbed)		
	Mercaptoethanol	-0.27	-0.25		
	TDMAT	-0.43	-		
	O ₂	-0.10	-2.13		
	H ₂ O	-0.15	-		
MoS ₂ Double S Vacancy (Figure S4c)		Top S Vacancy (Physisorbed)	In S Vacancy (Chemisorbed)	In S Vacancy (dissociated)	
	Mercaptoethanol	-0.25	-2.43 -1.39 (thiol chain)	-	
	TDMAT	-0.46	-	-	
	O ₂	-0.08	-2.30	-7.94	
	H ₂ O	-0.15	-	-	
MoS ₂ Line Vacancy (Figure S4d)		Top Vacancy (Physisorbed)	In Vacancy (Chemisorbed)	In S Vacancy (dissociated)	
	Mercaptoethanol	-0.69	-2.67	-	
	TDMAT	-0.86	-	-	
	O ₂	-0.19	-1.69	-7.73	
	H ₂ O	-0.62	-0.86		

gap of pristine MoS₂ calculated in the generalized gradient approximation is 1.62 eV (Figure 7a), in good agreement with previously published works.^{45,46} Although GGA is known to underestimate the true band gap, trends in changes to the band gap are preserved. To study the effects of S vacancies on the electronic structure, we compare the density of states of pristine and vacancy-containing MoS₂ with and without ME adsorption. A single isolated vacancy introduces a localized state below the conduction band (Figure 7b). The double sulfur vacancy introduces several states below the conduction band (Figure 7c), while the extended line vacancy results in a drastically altered band structure where the band gap is

reduced to 0.37 eV (Figure 7d). ME adsorption on the pristine surface does not alter the electronic properties significantly (Figure 7e), but Figure 7f shows that ME chemisorbed in a single sulfur vacancy removes the gap state and completely passivates the vacancy. However, ME bonding to the double (Figure 7g) or line vacancy (Figure 7h) cannot fully passivate the vacancy and does not remove the gap states.

Table 2. Adsorption energies of mercaptoethanol and TDMAT on O₂-MoS₂ surfaces. The surfaces considered are an S₂ vacancy with a chemisorbed O₂ molecule (Figure S4e), an S₂ vacancy with substitutional oxygen resulting from O₂ dissociation (Figure S4f), and “functionalized” surfaces whereby one oxygen atom adsorbs on the surface after dissociation (Figure S4g,h).

Surface	Molecule	Adsorption Energy on Site (eV)	
MoS ₂ S ₂ Vacancy-O ₂ Molecule (Figure S4e)		Top O ₂	
	Mercaptoethanol	-0.15	
	TDMAT	-0.39	
MoS ₂ S ₂ Vacancy-O ₂ Substitution (Figure S4f)		Top O	Bridge
	Mercaptoethanol	-0.28	-0.29
	TDMAT	-0.45	-
MoS ₂ S Vacancy-O Functionalized (Figure S4g)		Top Substitutional O	On Adsorbed O
	Mercaptoethanol	-0.37	-0.07
	TDMAT	-	-0.17
MoS ₂ S ₂ Vacancy-O Functionalized (Figure S4h)		Top Substitutional O	On Adsorbed O
	Mercaptoethanol	-0.34	-0.07
	TDMAT	-	-0.24

Our DFT results indicate that oxygen adsorption on sulfur vacancies is energetically favorable. Investigation of the electronic properties of the O₂-MoS₂ systems can therefore indicate which, if any, vacancy-containing surfaces are suitable for electronic device purposes. Oxygen interacts most easily with the S₂ vacancy. Physisorbed O₂ above the vacancy does not alter the density of states, leaving the gap states present. The O₂ molecule can overcome a small energy barrier (~0.1 eV) to bond in the S₂ vacancy (Figure S4e). The double vacancy is not fully passivated in this state, and gap states are present below the conduction band (Figure 8a). However, the dissociation of the O₂ molecule in the S₂ vacancy results in the removal of the gap states (Figure 8b). ME adsorption on top of the chemisorbed O₂ molecule (Figure S4e) introduces a localized state at the top of the valence band (Figure 8c), and the gap states are still present. However, when ME is allowed to chemisorb in the S vacancy neighboring the O₂ molecule (Figure S4f), both the localized valence state and the gap states are removed (Figure 8d). When ME adsorbs on

dissociated oxygen-MoS₂ surfaces (Figure S4g,h), a localized state is present at the top of the valence band (Figure 8e,f).

DISCUSSION

It is well known that ALD of metal oxides on pristine, untreated MoS₂ surfaces typically results in poor quality films that are not fully coalesced.^{11–19} This necessitates the use of seeding approaches to modify the surface energy and consequently its reactivity. Self-assembled monolayer (SAM) type approaches are quite popular as they rely on self-assembly that can be accomplished in exposure times ranging from a few minutes to several hours. Thiols are commonly used SAM molecules and have been used on MoS₂ surfaces as they are expected to interact with the -S terminated surface or sulfur vacancies.^{20,21,23–34} One such thiol, mercaptoethanol (that has an -OH terminal group) is used in this work to promote the growth of TiO₂ ALD films on MoS₂. However, the results

presented here suggest that a simple ME vapor treatment is not sufficient to improve film nucleation. DFT calculations indicate that ME adsorption on the pristine MoS₂ surface is weak. Coupled with XPS analysis of the as-received CVD MoS₂ starting surfaces that indicates a low (~5%) concentration of sulfur defects, these facts explain the formation of non-continuous ALD films on ME-treated MoS₂. This observation points out that an increased concentration of surface defect sites may be required to achieve uniform film growth. Sputtering the MoS₂ surface with argon ions is used to produce increased concentrations (~10–35%) of sulfur vacancies and *in situ* XPS during ion bombardment shows that the S:Mo ratio decreases with sputtering time (Figure 2), indicating that sulfur is preferentially removed during ion-

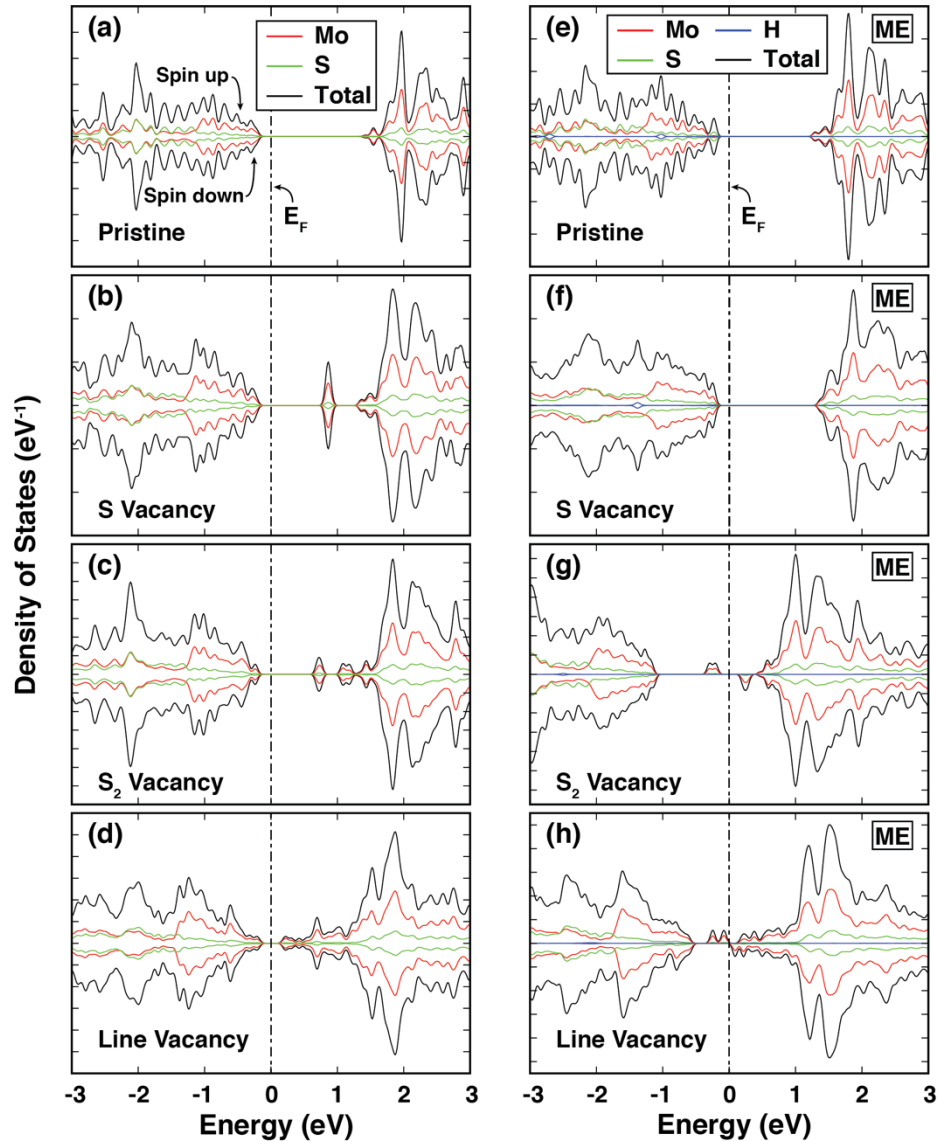


Figure 7. Spin-polarized density of states of (a) pristine MoS₂, (b) MoS₂ with a single S vacancy, (c) MoS₂ with a double S vacancy, and (d) MoS₂ with a line vacancy. Also shown are (e) ME on pristine MoS₂, (f) ME in a single S vacancy, (g) ME in a double S vacancy, and (h) ME in a line vacancy.

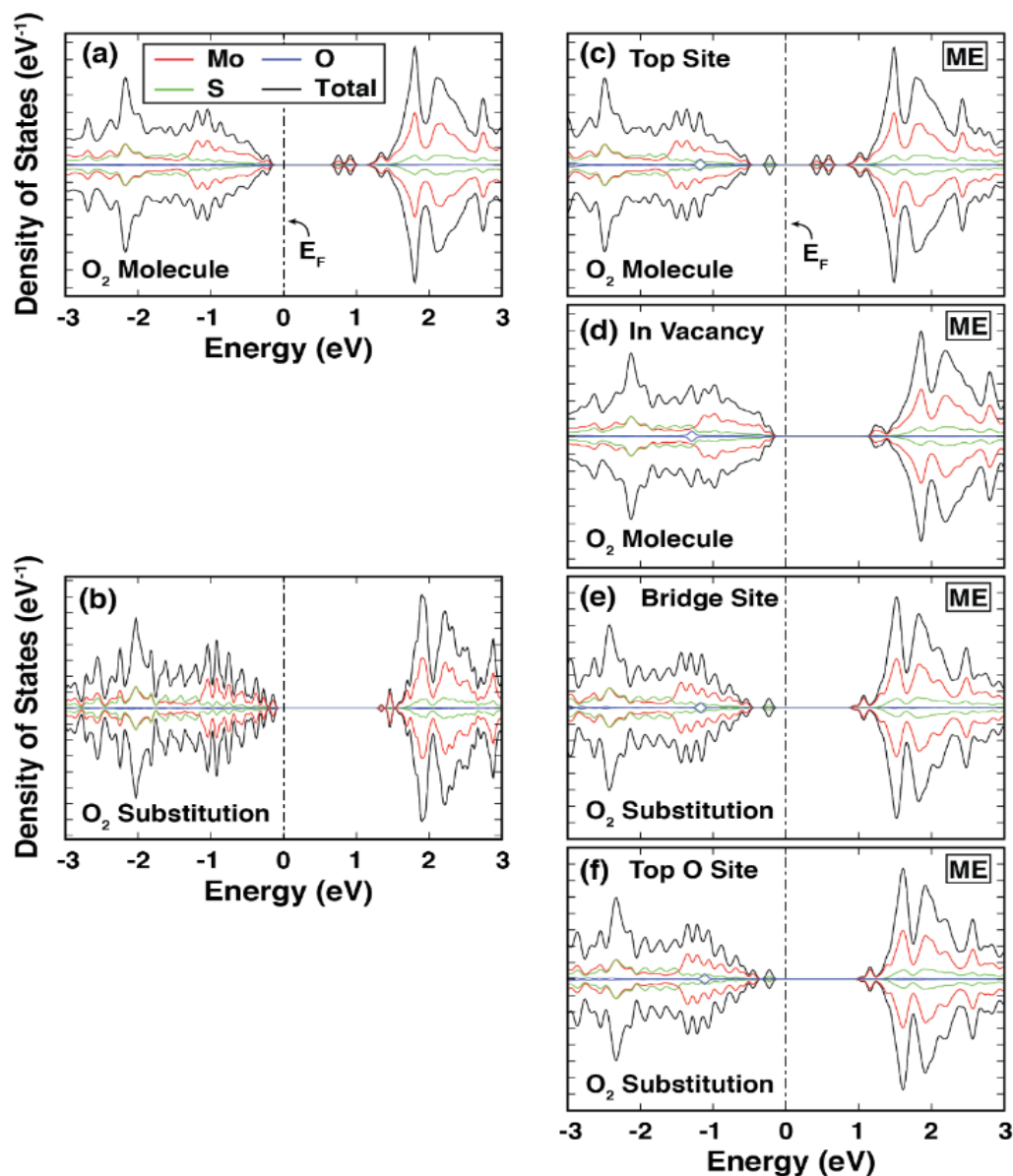


Figure 8. Spin-polarized density of states of an O_2 molecule (a) adsorbed in a double sulfur vacancy and (b) dissociated in a double sulfur vacancy (O atoms substitute for the missing S atoms). Also shown are the spin-polarized density of states of an ME molecule adsorbed on the O_2 - MoS_2 surface on (c) the top site of O_2 and (d) the vacancy next to O_2 . On the dissociated O_2 molecule, the density of states is shown for ME on (e) the bridge site between O atoms and (f) on the top site of one O atom. The ME molecule introduces a localized state just below the valence band.

beam irradiation. Importantly, the XPS measurements do not show any noticeable changes in peak shapes for the Mo 3d and S 2p regions (Figure 3) which indicate that the ion bombardment does not destroy the surface geometry. After treating these samples with ME, ALD of TiO_2 films results in uniform film growth, with no visible pinholes or gaps. However, sputtered samples that were not treated with ME show very similar film morphology (Figure 4) indicating that the ALD precursors may react with the untreated defect rich surface without the need of a seeding layer.

Possible Growth Mechanisms

Sulfur vacancies are known to be reactive and are expected to be passivated with oxygen or other species.^{40–44,47–52} As the samples were exposed to air for a few minutes after removal from the XPS chamber, it is conceivable that the sulfur defects have reacted with atmospheric components such as O_2 and moisture producing surface termination that may facilitate interaction with the TDMAT precursor and result in uniform

film growth. We investigate several possible mechanisms for the involvement of all these species in the surface reactions of untreated, vacancy-containing MoS₂, including adsorption on sulfur vacancies. The O₂ adsorption energy on a single S vacancy is calculated as -0.09 eV, indicating weak physisorption. It has been shown previously that oxygen may chemisorb strongly in the single S vacancy, and may do so dissociatively.^{41–44,49,50} However, in order for molecular oxygen to transition from the physisorbed state to the chemisorbed state in a single S vacancy, it must overcome an energy barrier of 0.74 eV, for which the transition time is estimated to be ~20 h.⁴¹ To reach the dissociated state where one oxygen atom fills the S vacancy and one oxygen adsorbs on a nearby S atom, another energy barrier of 0.8–0.93 eV must be overcome.^{43,44} Though dissociative adsorption of O₂ would leave adsorbed oxygen atoms on the surface which are known to seed ALD films,¹² this pathway is unlikely for single vacancies as our MoS₂ samples were exposed to air for just a few minutes at most as they were transferred from the glove box into the ALD chamber. Adsorption of H₂O is also equally unlikely ($E_{ads} = -0.15$ eV) on the single S vacancy. Based on the above, we expect that single sulfur vacancies remain unpassivated and reactive prior to thiol treatment and ALD. Conversely, the double S₂ vacancies are more reactive to oxygen and other species. O₂ may bind strongly with a double vacancy after overcoming a small energy barrier of ~0.1 eV. The dissociation of the O₂ molecule in the S₂ vacancy (whereby an oxygen atom is substituted in each S vacancy) is found to be energetically favorable.

Calculations of TDMAT adsorption on the single S vacancy show that the interaction between TDMAT and the vacancy-containing MoS₂ layer is strong ($E_{ads} = -0.43$ eV), and AIMD simulations at 600 K do not result in desorption of the TDMAT molecule. Calculations of TDMAT adsorption on double sulfur vacancies result in similar adsorption energies, and adsorption on line vacancies results in even stronger interaction ($E_{ads} = -0.86$ eV). Therefore, TDMAT adsorption on sulfur vacancies is another possible pathway of seeding TiO₂ film growth on defect-rich MoS₂ surfaces such as those seen in Figure 4g-i. The weak interaction of O₂ and H₂O with the single S vacancy suggests that adsorption of these molecules on single vacancies is unlikely, but adsorption of O₂ molecules on extended vacancies is expected as a result of their strong binding with double S and line vacancies. Although oxygen may fill the extended vacancies easily, TDMAT adsorption on oxygen-containing vacancies remains strong. Thus, improved TDMAT adsorption on vacancy-containing MoS₂ is the likely mechanism behind the uniform film growth observed in Figure 4g-i.

DFT studies indicate that ME may physisorb on single sulfur vacancies with $E_{ads} = -0.25$ eV, but the thiol chain can bind in a chemisorbed state ($E_{ads} = -1.49$ eV, Table S1). The chemisorbed thiol can seed TiO₂ film growth as it is -OH terminated and will react with TDMAT. ME is found to interact more strongly with a double vacancy or an extended line vacancy. In this case, the S-H bond is broken, and the thiol chain and H atom occupy neighboring vacancies, and the

thiol binds strongly ($E_{ads} = -1.39$ eV). AIMD indicates that this structure is stable at high temperature (600 K), and therefore functionalization of extended vacancies with ME may be a possible pathway for the smooth film growth observed in Figure 4a-c. Likewise, ME adsorption strength is either the same or slightly lowered on O₂-MoS₂ surfaces, indicating that ME adsorption is still possible as a seed layer on these surfaces. While the presence of ME is not required for this precursor this may not be the case for other precursor types, and as we demonstrate below, ME is required to preserve the electronic properties of the surface.

Furthermore, at the low deposition temperature used here (100°C), some precursor condensation on the pristine surface is expected. Condensation alone is not sufficient to promote smooth film growth, as evidenced by the pinhole-containing films in Figure 1a,b, but we expect that the smooth films seen in Figure 4g-i are a result of a convolution of TDMAT condensation and TDMAT adsorption on S vacancies. This result should be applicable to all precursors of the same alkylamine family but whether it applies to other ALD precursor families should be investigated separately. Based on these results, the smooth film growth on ME-treated surfaces (Figure 4a-c) results from a combined effect of precursor condensation, TDMAT adsorption on sulfur vacancies, and TDMAT reaction with adsorbed ME or oxygen.

Electronic Properties of Defective MoS₂

While a smooth oxide layer is important for device applications, the question remains as to the usefulness of defective MoS₂ for electronic devices. DFT calculations of the electronic structure show that formation of S vacancies introduces localized states into the band gap of the MoS₂ monolayer (Figure 7b-d). These gap states can trap or scatter charge carriers and decrease the charge carrier mobility. An approach to mitigate this is required for successful device engineering. ME reacts strongly with the vacancies and provides a pathway for the removal of the gap states. However, this is possible only for single vacancies. (Figure 7g,h). For extended vacancies, the adsorbed thiol molecule introduces spin-dependent gap states above and below the Fermi level. While the chemisorbed thiol chain can passivate the S vacancy that it occupies, the H atom occupying the neighboring site can not satisfy the dangling bonds left by the absence of a sulfur atom. Likewise, O₂ and H₂O cannot fully passivate the double S vacancy (except in the case of O₂ dissociation) and leave the system with less than desirable electronic properties. Our results suggest that there is a delicate balance between increasing surface reactivity via defect engineering and preserving the electronic properties of the channel material. ME treatment alone is not sufficient to produce smooth ALD films, and the introduction of gap states by extended vacancies cannot be mitigated by the same treatment. Therefore, the creation of vacancies should be carefully controlled as to avoid significant extended defects. It is possible that other treatments may yield improved results.

Interactions between molecular oxygen and extended sulfur vacancies are likely to occur. The calculations performed here

indicate that TDMAT adsorption should not be affected by oxygen filling of sulfur vacancies, and that ME adsorption may still occur on these surfaces. While oxygen dissociation in a double sulfur vacancy may remove the gap states and promote TDMAT adsorption, oxygen adsorption does not fully passivate the gap states without dissociation (Figure 8a-b). In the case of O₂ chemisorption, ME may still fill the second sulfur vacancy and heal the remaining gap states. In all cases of ME adsorption on O₂-MoS₂, the ME molecule introduces a localized state just below the top of the valence band. In this situation, the band gap is not drastically altered and so the desirable electronic properties of MoS₂ are preserved.

While perfect passivation of sulfur vacancies may not be feasible, careful engineering of the sulfur vacancy concentration along with O₂/ME saturation can restore the desired band gap properties while providing a favorable surface for TDMAT adsorption and thus TiO₂ film growth. Previous works have shown that encapsulating the MoS₂ layer with a high-k dielectric material increases charge carrier mobility,⁵³⁻⁵⁵ and such effects may result from O₂ saturation. Additionally, some of the damaging effects of surface vacancies may be mitigated in systems of bi-layer or tri-layer MoS₂, as has been reported for devices formed using plasma-enhanced ALD.⁵⁶

CONCLUSIONS

In this manuscript, we present a combined experimental and theoretical investigation of the interaction of TDMAT with MoS₂ surfaces. We find that TDMAT interacts very weakly with the pristine MoS₂ surface resulting in films with many pinholes for nominal thickness up to 6 nm. We hypothesized that ME could be used to seed the film growth on the MoS₂ surface, but experiments showed poor surface coverage. Calculations indicated that ME interacts weakly with the MoS₂ surface but may interact more strongly with the naturally occurring sulfur vacancies. Ar ion beam irradiation was used to increase the sulfur vacancy density on the MoS₂ surface and subsequent deposition on both untreated and ME treated samples showed complete surface coverage. The calculation indicated that TDMAT interacts directly with single and extended sulfur vacancies without the need for ME seeding. However, the creation of the vacancies results in the introduction of gap states that the ME treatment can passivate completely for the single vacancies and to a very large extent for the double and line vacancies. As a result, we provide a pathway for the deposition of high quality ALD dielectrics on the MoS₂ surfaces, which is required for the successful integration of these 2D materials in functional devices.

EXPERIMENTAL METHODS

Monolayer MoS₂ samples are grown on 280 nm Si/SiO₂ substrates via CVD using solid precursors. Molybdenum trioxide (MoO₃) and sulfur (S) powder are placed into a 3" 3-zone tube furnace in a 1:8 ratio. The substrates are suspended face-down above 0.05g MoO₃ using a quartz stage and placed in the center zone of the furnace. The S powder is placed in the upstream zone. The growth is conducted at atmospheric pressure, but prior to beginning the temperature ramp, 500 sccm of argon is flowed as a carrier gas. The center zone is

heated to 730 °C and the upstream zone is heated to 200 °C during the growth process ramp phase. The growth lasts for ~10 min. After the growth, the furnace is allowed to naturally cool to 50 °C before retrieving the samples. Samples are examined using an optical microscope and a Horiba Raman Confocal Imaging Microscope to confirm the presence of monolayer MoS₂.

ALD of TiO₂ films is performed at 100°C using tetrakis dimethylamino titanium (TDMAT) and water as precursors. The deposition is performed in a custom-built ALD reactor previously described by Henegar and Gougousi.⁵⁷ Both precursors are introduced by short pulses under nitrogen flow. TDMAT and water pulses are separated by a 30 s nitrogen purge. Spectroscopic ellipsometer measurements (J.A. Woollam α-SE) performed on a companion native oxide Si(100) sample showed that the TiO₂ film thickness is ~6.5 nm. The deposition consists of 100 ALD cycles for a nominal film thickness of 6 nm. After ALD, the TiO₂ film morphologies are analyzed via atomic force microscopy (AFM) using a Veeco Dimension 3100 AFM. The AFM images are processed using the WSXM software package.⁵⁸

Mercaptoethanol (SHCH₂CH₂OH) treatment of MoS₂ samples is performed by fixing the samples to the underside of the cap of a vial containing 200 μL of pure mercaptoethanol liquid. The vials are sealed and left at room temperature for 3 hours. This thiol treatment is performed in a glove box under nitrogen atmosphere to avoid atmospheric contamination.

The MoS₂ samples are sputtered at an accelerating voltage of 700 V, and XPS data are taken in-situ to monitor the sulfur concentration. Argon ion sputtering is performed under high vacuum at an accelerating voltage of 700 eV for 60-390 s using a Physical Electronics 04-303 differentially pumped ion gun. The sputter current is measured at ~100 nA. The ion fluence is calculated as $F = It/qA$, where I is the sputter current, t is the sputtering time, q is the elementary electron charge, and A is the area of sputtering. X-ray photoelectron spectroscopy (XPS) data are taken *in situ* using a Kratos AXIS 165 spectrometer with an Al monochromatic x-ray source (1486.6 eV). The resulting spectra are shifted to the C 1s peak at 284.8 eV, and the S:Mo ratios R are calculated by fitting the integrated peak areas of the S 2p and Mo 3d peaks, $A(S\ 2p)$ and $A(Mo\ 3d)$, respectively, as

$$R = \frac{A(S\ 2p)}{A(Mo\ 3d)} \quad (1)$$

The peak areas are corrected for the difference in relative sensitivity factor. This ratio can be used to find the fraction of sulfur vacancies as $V_s = 1 - R/2$. Since argon ion sputtering only creates vacancies on the top side of the MoS₂ monolayer, the fraction of sulfur vacancies (considering only the top side) is doubled to $V_s = 2 - R$. However, since the as-grown MoS₂ crystal contains some natural vacancies, this expression is modified to be

$$V_s = 2 - R - V_{s,0}/2 \quad (2)$$

where $V_{s,0}$ is the naturally occurring vacancy concentration. Here, we estimate $V_{s,0} \approx 0.05$ from XPS analysis of the starting MoS₂ surfaces.

After sputtering, samples are removed from the XPS chamber under nitrogen atmosphere and sealed in vials to prevent air exposure. The vials are transferred to a nitrogen-filled glove box where select samples are treated with mercaptoethanol as described previously. The vials are resealed under N₂ atmosphere and left for 3 hours. After removal from the vials, the MoS₂ samples are transferred immediately to the ALD reactor. A control set of samples is prepared in the same manner, but without the thiol vapor treatment.

COMPUTATIONAL METHODS

Density functional theory (DFT) calculations are performed using the Vienna Ab initio Simulation Package (VASP).⁵⁹ Calculations are carried out within the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof (PBE).⁶⁰ A cutoff energy of 520 eV and total energy convergence of 10^{-5} eV is used for all calculations. Sulfur vacancy concentrations are adjusted by placing a single vacancy in a $2\times 2\times 1$, $3\times 3\times 1$, or $4\times 4\times 1$ supercell corresponding to vacancy concentrations (on the top side) of 25%, 11%, and 6%, respectively. K-points are generated in a gamma-centered mesh of $9\times 9\times 1$, $6\times 6\times 1$, or $5\times 5\times 1$ for the $2\times 2\times 1$, $3\times 3\times 1$, or $4\times 4\times 1$ supercells, respectively. Double sulfur vacancies are calculated in $6\times 6\times 1$ supercells with a k-point mesh of $3\times 3\times 1$ and line vacancies are calculated in rectangular $4\times 4\times 1$ supercells with a k-point mesh of $3\times 5\times 1$. All calculations include spin polarization effects. Calculations of the adsorption energy of molecules on the MoS₂ surface are performed by placing the molecule ~ 2 Å above the MoS₂ layer and allowing the system to relax. The adsorption energy of a molecule on the surface or sulfur vacancy is calculated as

$$E_{ads} = E(Mol + MoS_2) - E(Mol) - E(MoS_2) \quad (3)$$

where $E(Mol+MoS_2)$ is the total energy of the combined system, $E(Mol)$ is the total energy of the isolated molecule, and $E(MoS_2)$ is the total energy of the isolated MoS₂ layer. The energy barrier for ME, H₂O, or O₂ molecules binding to a sulfur double vacancy in MoS₂ is calculated by fixing the molecule between 3 Å and 0 Å above the surface at 0.5 Å intervals. At each interval, only one atom in the molecule was fixed and all other atoms are allowed to relax fully. In these calculations, one Mo atom in the MoS₂ layer is fixed to prevent translation (in the vacuum direction) of the layer. When the molecule is placed in the vacancy, all atoms are allowed to relax.

Ab initio molecular dynamics (AIMD) simulations are performed using VASP to determine the dynamical stability of several molecule-MoS₂ systems. The simulations are performed at a temperature of 600 K with a timestep of 0.5 fs and run for 2000 steps (1 ps total) using the Nosé-Hoover^{61,62} thermostat to obtain the canonical (NVT) ensemble.

The cluster expansion method implemented using the Alloy Theoretic Automated Toolkit (ATAT)⁶³ is used to generate MoS₂ structures containing sulfur vacancies in concentrations from 0-100 percent (on a single side). The results from the cluster expansion are used to find the most energetically favorable vacancy-containing structures at the desired concentrations of ~ 10 -40 percent. Further details of the simulations are included in the Supporting Information and the energetics of all structures are shown in Figure S1.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

The Supporting Information contains details about the cluster expansion calculations and example images of vacancy-containing MoS₂ structures generated by cluster expansion. Also included are images of MoS₂ and O₂-MoS₂ surfaces used in simulations of molecule adsorption and the description and energetics of ME adsorption on bare MoS₂ and S Vacancies.

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