HfO$_2$ on UV–O$_3$ exposed transition metal dichalcogenides: interfacial reactions study

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Abstract

The surface chemistry of MoS$_2$, WSe$_2$ and MoSe$_2$ upon ultraviolet (UV)–O$_3$ exposure was studied in situ by x-ray photoelectron spectroscopy (XPS). Differences in reactivity of these transition metal dichalcogenides (TMDs) towards oxidation during UV–O$_3$ were observed and correlated with density functional theory calculations. Also, sequential HfO$_2$ depositions were performed by atomic layer deposition (ALD) while the interfacial reactions were monitored by XPS. It is found that the surface oxides generated on MoSe$_2$ and WSe$_2$ during UV–O$_3$ exposure were reduced by the ALD process (‘self-cleaning effect’). The effectiveness of the oxide reduction on these TMDs is discussed and correlated with the HfO$_2$ film uniformity.

Introduction

Two-dimensional transition metal dichalcogenides (TMDs), as part of the mono- and few-layer materials library, have potentially exceptional properties such as dangling bond-free surfaces and thickness-tunable band gap energies [1, 2], making them outstanding candidates as channel materials for beyond Si-CMOS device structures [3]. The electronic and optoelectronic properties of MoS$_2$, a readily available material in nature, have been extensively studied in recent years [4]. However, the presence of a Schottky barrier at the metal/MoS$_2$ interface has limited the MoS$_2$-based field-effect transistors (FETs) performance [5]. Moving forward into the exploration of other members in the TMD library, several efforts have focused on studying 2D WSe$_2$, where field-effect mobility ($\mu_{\text{FE}}$) values up to ~500 cm$^2$ V$^{-1}$ s$^{-1}$ have been reported [6]. Furthermore, band–band tunneling properties of WSe$_2$ for tunnel FET applications have been demonstrated [7]. Following these efforts, MoSe$_2$ has been implemented in FETs, exhibiting a promising performance (i.e. $\mu_{\text{FE}}$ ~ 150–200 eV) according to recent reports [8, 9]. It has been demonstrated theoretically [10] and experimentally [11–13] that the limiting effect on mobility associated with Coulomb scattering can be reduced by having a dielectric material on the 2D channel, motivating several studies related to dielectrics on TMDs. However, it has also been shown that, given the relative inertness of the TMDs surfaces, the direct atomic layer deposition (ALD) of high-κ dielectrics on clean, un-treated surfaces results in the formation of clusters or islands instead of continuous films[14, 15]. Previously, it was shown that uniform, pin-hole free and thin (~4 nm) Al$_2$O$_3$ films can be obtained by performing a ultraviolet (UV)–O$_3$ surface pre-treatment on MoS$_2$, where covalent oxygen functionalization of the MoS$_2$ top-most sulfur layer occurred, while avoiding molybdenum oxidation [16]. Alternative processes have been reported in order to improve the ALD high-κ nucleation on MoS$_2$ such as oxygen plasma pre-treatment [15], the use of ozone as an oxidant precursor during ALD of Al$_2$O$_3$ [17], and metal-oxide seed layers [18].

Yet, whether the proposed processes can be directly extended to other TMDs remains an important question, since different compositions could result in variation of surface properties. Here, in situ monochromatic x-ray photoelectron spectroscopy (XPS) studies were used to characterize the effect of a UV–ozone treatment of MoSe$_2$ and WSe$_2$ single crystal surfaces. Also, the surface reactivity towards oxidation of these TMDs was compared and modeled by density functional theory (DFT) calculations. It was
found that surface oxides formed upon UV–O₃ exposure of the diselenides surface. Additionally, XPS monitored the interfacial chemistry between ALD-HfO₂ and the UV–O₃ treated TMD surfaces. Finally, the HfO₂ film uniformity on the UV–O₃ treated TMDs was investigated and correlated with the interfacial chemistry.

**Experimental details**

The UV–O₃ treatments and ALD studies described here were performed in situ using an ultrahigh vacuum (UHV) cluster tool described elsewhere [19]. XPS was carried out using a monochromated Al Kα x-ray source (hν = 1486.7 eV) and equipped with a seven channel analyzer, using a 15 eV pass energy. The XPS peak deconvolution was achieved with the software Analyzr™ [20], using Voigt functions with independent control of the Lorentzian and Gaussian components, and applying a dynamic Shirley background subtraction. The top-most layers from MoS₂ (SPI Supplies), MoSe₂ (2D Materials) and WSe₂ (Nanoscience Instruments) bulk crystals (all (0001) orientation) were mechanically exfoliated using Scotch® Magic™ tape, and the freshly as-exfoliated bulk materials were loaded immediately into UHV. All the UV–O₃ exposures were performed at room temperature as described in [16]. In an interconnected chamber, the sample surfaces are placed within a few mm from a UV lamp (low pressure mercury lamp) in the presence of O₂ (O₂ partial pressure 10 mbar). After analysis, the samples were transported back to the ALD reactor for further processing. The sequential UV–O₃ exposure to MoS₂, a room temperature UV–O₃ treatment was performed on WSe₂ and MoSe₂, while MoS₂ was also used as a control sample for comparison with previous work [16]. XPS spectra of MoS₂, MoSe₂, and WSe₂, after 3, 6 and 15 min of UV–O₃ exposure, is shown in figures 1(a)–(c) respectively, while table 1 summarizes the bonds formed after UV–O₃, showing their binding energy (BE) and ratios of the integrated intensity of the corresponding peaks with respect to the bulk signal. The sequential UV–O₃ exposure on MoS₂ shows that S–O bond formation is detected after 3 min, and by increasing the exposure time, i.e. 6 and 15 min, the oxygen adsorption saturates to form 1 ML [16]. Under these conditions, no Mo–O bond formation is detected, as previously reported. It has also been reported that UV–O₃ can cause molybdenum oxidation in MoS₂, when the exposure is much longer (60 min) [29]. This implies that the oxidation process is dose and time dependent.

In the case of MoSe₂, the 3 min UV–O₃ exposure initially results in the formation of Se–O bonding, without causing Mo oxidation. The nature of the Se–O results analogous to the S–O observed in MoS₂ [16], which may be described as chemisorbed oxygen on the surface, i.e. covalent bond formation between oxygen and the top most selenium layer, while preserving the covalent bonding within the MoSe₂ layer. However, in contrast to MoS₂, the 6 min UV–ozone exposure results in sub-stoichiometric molybdenum oxide (MoOₓ) formation. The MoO₃ peak shows a symmetric lineshape, suggesting that Mo is present in only one of the seven different phases that has been identified for MoOₓ, x = 2.75–3 [30, 31]. In the 3D Se region, the previously observed Se–O bond is below the detection limit, however, a new peak at ∼59 eV indicates...
that selenium is further oxidized forming a selenium sub-oxide SeO\textsubscript{x}. In addition, an extra feature at \(\sim 0.6\) eV higher in binding energy than the bulk MoSe\textsubscript{2} peak is observed in both Mo 3d and Se 3d core levels (blue peak in figure 1(b)).

Previous studies in MoS\textsubscript{2} correlated the appearance of peaks at higher BE from the main bulk peak, for both Mo 3d and S 2p, with the existence of molybdenum oxysulphide (MoS\textsubscript{x}O\textsubscript{y})\[32–34\], where the BE position of such peaks was dependent on the \(x\) and \(y\) values. A peak at a slightly higher BE (\(\sim 0.5–0.8\) eV) than the characteristic MoSe\textsubscript{2} peak in Se 3d could be also correlated with metallic Se \[35\], however, the fact that both core levels showed this high BE feature makes this chemical state assignment less probable. Another possible assignment could be a sub-stoichiometric MoSe\textsubscript{x} phase, however, the existence of MoSe\textsubscript{x} would cause the transition metal peak to shift lower in BE and the chalcogen peak to broaden \[36\], and this situation is not observed. Thus, the feature in blue in figure 1(b) is associated with MoSe\textsubscript{x}O\textsubscript{y} formation, caused by oxidation during UV–O\textsubscript{3} exposure. Finally, after UV–O\textsubscript{3} for 15 min, the MoO\textsubscript{x} peak shifted to 0.4 eV higher BE which is consistent with a higher oxygen content in MoO\textsubscript{x} \[30, 37\]. Also, the MoO\textsubscript{x} oxide to bulk peak intensity ratio increases in comparison to the 6 min ratio, showing that the oxygen is inserted deeper within the material. In the case of Se 3d, the sub-stoichiometric SeO\textsubscript{x} shows a shift to 0.4 eV higher BE, suggesting complete oxidation to SeO\textsubscript{2}.

In comparison, figure 1(c) shows the XPS spectra of WSe\textsubscript{2} for the same UV–O\textsubscript{3} exposure times. After UV–O\textsubscript{3} exposure for 3 and 6 min, Se–O bonding is detected however the Se–O to bulk WSe\textsubscript{2} peak intensity ratio is lower than that for MoSe\textsubscript{2}. W oxidation in the form of WO\textsubscript{x} is detected after 6 min of exposure. Similar to MoSe\textsubscript{2}, the UV–O\textsubscript{3} exposure of WSe\textsubscript{2} presents tungsten oxyselenide bonding (WSe\textsubscript{x}O\textsubscript{y}) after 15 min of exposure, in addition to WO\textsubscript{x} and SeO\textsubscript{x} formation.

Oxidation studies of these TMDs in the bulk form were performed previously by Jaegermann, et al \[38\], where reactivity towards oxidation was found to go from lower to higher in the sequence:

Table 1. Chemical species detected on MoSe\textsubscript{2}, WSe\textsubscript{2} and MoS\textsubscript{2} after different UV–O\textsubscript{3} exposure times, showing the corresponding peak positions in eV and their integrated intensity ratio with respect to the bulk peak (shown in brackets \('[\text{]}\)\).

| UV–O\textsubscript{3} treatment time (min) | 3 min | 6 min | 15 min |
|-----------------------------------------|-------|-------|--------|
| S 2p                                    | S–O 162.9 [0.06] | S–O 162.9 [0.1] | S–O 162.9 [0.1] |
| MoS\textsubscript{2} Mo 3d               | —     | —     | —      |
| Se 3d                                   | S–O 56.3 [0.04] | S–O 56.3 [0.05] | S–O 56.3 [0.05] |
| MoSe\textsubscript{2} Mo 3d              | —     | —     | —      |
| Se 3d                                   | —     | —     | —      |
| WSe\textsubscript{2} W 4f                | —     | —     | —      |

Figure 1. XPS spectra of the initial as-exfoliated surface and after 3 min, 6 min and 15 min of UV–O\textsubscript{3} exposure for (a) MoS\textsubscript{2} (Mo 3d, S 2p), (b) MoSe\textsubscript{2} (Mo 3d, Se 3d) and (c) WSe\textsubscript{2} (Se 3d, W 4f). Optimized (d) MoS\textsubscript{2}, (e) MoSe\textsubscript{2} and (f) WSe\textsubscript{2} structures after oxygen adsorption on top of the chalcogen atom (top view) and after replacement of the chalcogen atom with an oxygen atom (tilted top view).
MoS$_2$ < MoSe$_2$ < WSe$_2$. This tendency was related to the degree of mixed metal d-states from the transition metal with the p-states in the chalcogenide, based on ionization energies arguments. However, the focus of that study was the photoelectrochemical oxidation in solution, using electrolytes (i.e. K$_2$SO$_4$) as oxidizers, which might introduce additional variables in the oxidation processes. Thus, DFT calculations were performed in order to have a better understanding of the energetics involved in the oxidation of TMDs.

Figures 1(d)–(f) shows optimized structures for MoS$_2$, MoSe$_2$ and WSe$_2$, respectively, when an oxygen atom is adsorbed on top of the chalcogen (O–Se, O–S) and when oxygen substituted the chalcogen to form a transition metal–oxygen bond (O–Mo, O–W). The calculated formation energies of the oxygen adsorption and chalcogen substitution with oxygen are listed in table 2, which were obtained using the following equation:

$$E_{\text{form}} = E(\text{O}: MX_2) - E(\text{pristine})$$

$$= \mu_{\text{O}} + \mu_{\text{S}}$$

(1)

where $E_{\text{form}}$ is the formation energy of the adsorbed or substitutional oxygen on MX$_2$ surfaces with total DFT energy $E(\text{O}: MX_2)$, $E$ (pristine) is the DFT energy of the pristine MX$_2$ surfaces ($M = W$ or Mo and $X = S$, Se), $\mu_{\text{O}}$ and $\mu_{\text{S}}$ are the reference chemical potentials of O (oxygen molecule) and S (bulk sulfur) and $n$ is the number of adsorption or substitutional O atoms. Under this definition, negative values of the formation energy refer to thermodynamically stable oxidation process.

According to the formation energies shown in table 2, O–S bond formation in MoS$_2$ is more energetically favorable and therefore more stable in comparison to O–Se in MoSe$_2$ and WSe$_2$. The DFT calculations also indicate that oxygen desorption will occur more easily in MoSe$_2$ and WSe$_2$, in comparison to MoS$_2$. The formation energy required for the replacement of the chalcogen to form a direct bond between oxygen and the transition metal is found to be more energetically favorable in the case of MoSe$_2$ and WSe$_2$ than for MoS$_2$, which is consistent with the XPS results after UV–O$_3$ exposure. The relative lower stability of the O–Se bond in comparison to O–S implies that desorption of oxygen, and possibly the ‘kick-out’ [39] of O–Se species, can leave unsaturated bonds for the transition metal, which then are readily available to form Mo–O and W–O bonds in presence of oxygen, such as during a UV–O$_3$ exposure. Experimentally, this oxidation process caused the formation surface oxides of 0.36 nm and 1 nm thickness in MoSe$_2$ for 6 min and 15 min of UV–O$_3$ exposure respectively, while the surface oxides in WSe$_2$ exhibited 0.33 nm and 0.66 nm thicknesses for the same mentioned exposure times, according with XPS thickness calculations.

These UV–O$_3$ exposure studies demonstrate that oxygen functionalization of MoSe$_2$ and WSe$_2$ surfaces is more difficult to control compared to MoS$_2$. Yet, the impact of having surface oxides on these TMDs prior to high-k dielectric deposition by ALD is still of interest. Thus, HfO$_2$ was sequentially deposited by ALD on the UV–O$_3$ treated MoSe$_2$ and WSe$_2$, while the interface chemistry was monitored by XPS. For comparison purposes, all the samples discussed here received a UV–O$_3$ exposure for 6 min.

Figure 2(a) shows that after one ALD cycle on functionalized MoSe$_2$, the MoO$_3$ peak intensity significantly decreases to ~24% of its initial intensity. In the Mo 3d region, a new peak is detected at 231.9 eV, which is designated as the Mo$^{5+}$ oxidation state [40], indicating that the Mo–O bonds are reduced (i.e. O was transferred to Hf, resulting a lower oxidation state of Mo). Additionally, the SeO$_2$ intensity decreases below the detection limit, as shown in the Se 3d region. The decrease in oxide intensity during precursor pulsing in ALD, or ‘self-cleaning’, effect was previously studied for III–V materials, such as In$_x$Ga$_{1-x}$As [41]. The self-cleaning reduction reactions that occurred after one cycle result in the gradual reduction of the oxidation state from Mo$^{6+}$ to Mo$^{5+}$. In addition, the fact that no Mo$^0$ or other chemical state was detected suggests that MoO$_3$ went through a ligand exchange reaction with the Hf precursor, forming a volatile molybdenum compound possibly of the form Mo(N(CH$_3$)$_2$)$_x$ [42]. Based on the thermodynamic quantities, HfO$_2$, with a Gibbs free-energy of formation of ~251.8 kcal mol$^{-1}$ [43], results in a more energetically favorable reaction product than MoO$_3$, assuming that the Gibbs free-energy of MoO$_3$ is close to—159.65 kcal mol$^{-1}$ [44], which is the corresponding value for MoO$_2$. For the Se 3d feature, no lower oxidation states are detected (i.e. S$^0$), indicating that SeO$_2$, a volatile compound, may be thermally desorbed from the surface in vapor phase [45]. Finally, the MoSe$_2$O$_x$ peak is not observed after one cycle, suggesting that the MoSe$_2$O$_y$ phase possibly recovers its initial state as MoSe$_2$ through the SeO$_2$ desorption channel, thus contributing to the bulk Se peak signal intensity.

Further deposition of HfO$_2$ using five ALD cycles results in a decrease of the Mo$^{6+}$ intensity to below the detection limit; only Mo$^{5+}$ remains. As shown in figure 2(b), the Mo$^{5+}$ to MoSe$_2$ integrated intensity ratio is ~0.03, suggesting that most of the surface
oxides undergo ‘self-cleaning’ reactions. The Se 3d spectra show no change after five cycles. After ten cycles, no interfacial oxides from MoSe₂ are detected, and further HfO₂ deposition only caused attenuation of the MoSe₂ features. Figure 3(c) shows that the chemical identity of HfO₂ remains constant through the sequential depositions.

In an analogous process, HfO₂ was sequentially deposited on UV–O₃ treated WSe₂ followed by XPS analysis. Figure 3(a) shows the evolution of WSe₂ oxides after sequential HfO₂ deposition by ALD. (b) The WOₓ (SeOₓ) to WSe₂ peak ratio, obtained from their respective integrated intensities. (c) Hf 4f spectra after 1, 5, 10 and 30 ALD cycles on UV–O₃ treated WSe₂. The inset in (c) shows the Hf 4f integrated intensity with respect to the number of ALD cycles.
chemical states through the experiment. It is shown that, in contrast to MoSe$_2$, the decrease in intensity of the transition metal oxide in WSe$_2$ is minimal after the first cycle. In fact, the WO$_x$ to bulk intensity ratio remains constant, however the Se–O intensity decreases below the detection limit, and the SeO$_x$ to WSe$_2$ ratio decreases by $\sim 44\%$. Also, the HfO$_2$ signal intensity after the first cycle of deposition on WSe$_2$ (figure 3(c)) is smaller in comparison to that obtained for MoSe$_2$ (figure 3(c)).

Even when the formation of HfO$_2$ is more energetically favorable than WO$_x$ based on the Gibbs free energy (WO$_3 \approx -195.7$ kcal mol$^{-1}$), WO$_x$ remains on the WSe$_2$ surface, exhibiting lower reactivity during the ALD ‘self-cleaning’ reduction reactions in comparison to MoO$_x$. Various hypotheses can be made to explain the limited HfO$_2$ growth. First, assuming a ligand exchange mechanism as in the case of MoSe$_2$, then dissociation of W–O bond would be needed. The dissociation energy of the W–O bond is $720 \pm 71$ kJ mol$^{-1}$, which is much higher than the Mo–O dissociation energy $597.2 \pm 33.5$ kJ mol$^{-1}$ thus the oxygen loss in WO$_x$ and subsequent formation of a volatile W(N(CH$_3$)$_3$)$_x$ compound requires a higher energy than MoO$_x$. Secondly, WO$_x$ and MoO$_x$ clusters are well known for their catalytic properties toward oxidation, where it was found that Mo$^{6+}$ will be more easily reduced to Mo$^{5+}$ than W$^{6+}$ to W$^{5+}$ due to the high stability of WO$_3$.[47] This is consistent with our observation in MoO$_x$ and WO$_x$ reactivity after one ALD cycle. The capability of WO$_x$ to remain in the W$^{6+}$ oxidation state makes WO$_x$ an effective oxidizing agent of organic molecules.[34]. Thus, another possible scenario is the reaction between WO$_x$ and the organic ligand in TDMA-Hf inhibiting ligand exchange reactions. In fact, from the Cls spectra, which overlap with a Se Auger feature, additional carbon species are detected in WSe$_2$ in comparison to MoSe$_2$ after the first cycle and subsequent cycles (see supplementary information (SI)).

After five cycles, the WO$_x$ to WSe$_2$ peak ratio decreases by only 5% along with a WO$_x$ peak shift to a lower BE of $\sim 0.2$ eV, while the SO$_x$ to WSe$_2$ peak ratio decreases by 31% from its previous value. Interestingly, extra features at identical lower BE positions from the bulk WSe$_2$ signals, for both W 4f and Se 3d are detected. The appearance of low BE peaks in WSe$_2$ was previously reported and attributed to a non-va

don der Waals surface, [48] characterized by edge planes and stepped surfaces. Such a non-homogeneous surface potential can give rise to different fermi level positioning, shifting the core levels in WSe$_2$ the same amount. Thus, these newly identified peaks can be identified as WSe$_2$ with a different fermi level in reference to the initial WSe$_2$. A non-va
ndon der Waals surface could be generated from desorption of surface oxides leaving regions in WSe$_2$ with unsaturated bonds and/or partially etched areas. After 30 ALD cycles, the SeO$_x$ is below the detection limit, and the WO$_x$ to WSe$_2$ peak intensity ratio decreases to a value of 0.08, with a final BE position $\sim 0.53$ eV lower than the initial WO$_x$ BE, due to lower oxygen content in WO$_x$.[49]. This indicates that lower oxygen content in WO$_x$ improves the rate of ligand exchange reactions between WO$_x$ and TDMA-Hf.

It should be noted that the Hf 4f integrated intensity is significantly different on MoSe$_2$ and WSe$_2$ for same number of cycles by comparing figures 2(c) and 3(c), where the final HfO$_2$ content on MoSe$_2$ is about three times that detected on WSe$_2$, suggesting differences in HfO$_2$ coverage. For such reasons, the surface topography of the HfO$_2$ films on the UV–O$_3$ exposed TMDs was also investigated by ex situ AFM. For comparison, HfO$_2$ was deposited (30 cycles of TDMA-Hf and H$_2$O) on as-exfoliated non-treated samples, where the dearth of reactive sites on the MoSe$_2$ and WSe$_2$ surfaces impeded uniform ALD nucleation, thus HfO$_2$ is deposited following an island-type growth mechanism, as observed on MoS$_2$.[14]. In contrast, on the UV–O$_3$ treated MoSe$_2$, the HfO$_2$ film is fully covered and pin-hole free (figure 4(a)). Therefore, the presence of surface oxides formed after UV–O$_3$ enhanced HfO$_2$ growth rate in comparison to non-treated MoSe$_2$, leaving as a result a completely covered HfO$_2$ film with a RMS roughness of only 0.15 nm. Interestingly, on the UV–O$_3$ treated WSe$_2$, HfO$_2$ islands with a triangular shape are formed with edge length and height in the range of 30–60 nm and 4–5 nm, respectively. It has been shown that triangular hole-like structures can be generated on WSe$_2$ by oxidative electrochemical etching promoted by AFM[50, 51] and STM[52, 53] tip-sample voltage. In this case, the presence of triangular hole-like structures on WSe$_2$ could have served as nucleation site for HfO$_2$, resulting in a quasi-ordered triangular cluster growth. This implies that oxidative etching of WSe$_2$ could have taken place during UV–O$_3$ exposure for 6 min and/or ALD self-cleaning reactions. In fact, the last hypothesis correlates with the newly detected WSe$_2$ XPS peaks (blue features in figure 3(a)) and in turn with the formation of a non-van der Waals surface, as discussed previously.

In accordance with the AFM results, cross-section STEM images in figure 5(a) shows a uniform HfO$_2$ film with thickness of $\sim 4$ nm on UV–O$_3$ treated MoSe$_2$, having a minimal variation in thickness across a length of 0.25 μm (see SI). Interestingly, the top-most MoSe$_2$ surface exhibits darker contrast regions that correspond to selenium-deficient MoSe$_2$ according to electron energy loss spectroscopy line scans across the HfO$_2$–MoSe$_2$ interface (shown in the SI). The ALD self-cleaning reactions occurred right at the MoSe$_2$ surface are likely to be involved in the generation of such selenium-deficient regions. It is also evident that the MoSe$_2$ layers below the darker contrast region are continuous and unaltered.

Finally, the high magnification STEM image in figure 5(b) gives further insights in regard to HfO$_2$ on
the UV–O$_3$ treated WSe$_2$. Partially etched WSe$_2$ layers are identified at the interface with the HfO$_2$ islands, which correlates with the XPS and AFM results described above. Here, the contrast from the partially etched WSe$_2$ layers is weaker at the HfO$_2$/WSe$_2$ interface than it is in the bulk WSe$_2$. This can be explained by considering that an STEM image is averaging cross-sectional information from a finite ∼100 nm thick material. Since the triangular hole-like structures observed in this work have an area smaller than the
thickness analyzed in cross-section by STEM, their presence could only be observed in STEM as a weakening of the contrast, while some signal from the unetched portions of that same layer will always be obtained. Clearly, various mechanisms are involved in the HfO$_2$ growth on UV–O$_3$ treated WSe$_2$. First, the presence of WO$_x$ on the WSe$_2$ surface and its relative high stability during self-cleaning reactions slows down the HfO$_2$ growth rate in comparison to MoSe$_2$ for same number of cycles, generating a partially covered HfO$_2$ film. Secondly, the presence of triangular hole-like structures on WSe$_2$ generated by etching caused the preferential HfO$_2$ nucleation on such structures, forming triangular HfO$_2$ islands.

Conclusions

In summary, it is found that selective oxygen functionalization of the selenium-based TMDs studied here is limited by highly energetically favorable oxidation of the transition metal. These results highlight the importance that the TMD composition has on the reactivity towards oxidation. The investigation of the ALD of HfO$_2$ on the TMDs with initial surface oxides elucidates self-cleaning reduction reactions and the desorption of volatile species during the ALD process. According to the interface study, the surface oxides on MoSe$_2$ are completely removed by the self-cleaning reduction reaction upon HfO$_2$ deposition. In contrast, the self-cleaning effect is less effective in the oxide removal on WSe$_2$ mainly due to the relative stability that WO$_x$ exhibits. Thus, the ability of assisting the HfO$_2$ nucleation is superior for MoO$_x$ than WO$_x$. Finally, the coverage of HfO$_2$ on the TMD surfaces was improved by the UV–O$_3$ pre-treatment.

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