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Mechanism of Thermal Atomic Layer Etch of W Metal Using Sequential Oxidation and Chlorination: A First-Principles Study

Suresh Kondati Natarajan,* Michael Nolan, Patrick Theofanis, Charles Mokhtarzadeh, and Scott B. Clendenning

ABSTRACT: Thermal atomic layer etch (ALE) of W metal can be achieved by sequential self-limiting oxidation and chlorination reactions at elevated temperatures. In this paper, we analyze the reaction mechanisms of W ALE using the first-principles simulation. We show that oxidizing agents such as O₂, O₃, and N₂O can be used to produce a WOₓ surface layer in the first step of an ALE process with oxygen being the most reactive. While the oxidation pulse on clean W is very exergonic, our study suggests that runaway oxidation of W is not thermodynamically favorable. In the second ALE pulse, WCl₆ and Cl₂ remove the oxidized surface W atoms by the formation of volatile tungsten oxychloride (WOₓClᵧ) species. In this pulse, each adsorbed WCl₆ molecule was found to remove one surface W atom with a moderate energy cost. Our calculations further show that the desorption of the additional etch products is endothermic by up to 4.7 eV. Our findings are consistent with the high temperatures needed to produce ALE in experiments. In total, our quantum chemical calculations have identified the lowest energy pathways for ALE of tungsten metal along with the most likely etch products, and these findings may help guide the development of improved etch reagents.

KEYWORDS: atomic layer etching, transistor contacts, density functional theory, self-limiting reaction, atomistic simulations, first principles

1. INTRODUCTION

Atomic layer etch (ALE) processing has gained considerable attention in recent years within the semiconductor industry. The continued scaling of semiconductor devices demands the use of ever-thinner and higher-performing materials, which drives the development of gentle etch process technologies with atomic-level precision and high degrees of selectivity toward surrounding materials. ALE shares many similarities with the well-known atomic layer deposition (ALD), widely used in the semiconductor industry, and can be considered as the reverse of ALD. ALE permits the removal of thin films layer by layer exploiting atomic-scale precision inherent in the method using sequential and self-limiting surface reactions, similar to ALD. Currently used ALE processes are anisotropic using directional high energy ion bombardment to drive the removal of the modified surface layers. On the other hand, a thermal ALE process relies on temperature and thermochemically favorable reactions to drive the removal of surface species. There are a multitude of examples for thermal ALE of various materials, including oxides (HfOₓ, ZrO₂, SiO₂, WOₓ, ZnO, and Al₂O₃), nitrides (including AlN, GaN, and TiN), fluorides (e.g., AlF₃), and some work on W. Other ALE techniques include plasma ALE of SiO₂, ZnO, and GaN, and infrared annealing ALE of SiN₄. Despite this effort, the atomistic details of the mechanism of thermal ALE processes are still not fully understood.

Tungsten, because of its low resistivity, resistance to electromigration, and ease of thin film growth by atomic layer and chemical vapor deposition, is often used in source/drain contacts in CMOS devices. Unlike ALD processes for W, which have received considerable attention, the utility of a complementary W atomic layer etch process has only recently emerged. Due to the continued scaling of critical dimensions in next-generation semiconductor devices and the incorporation of a more varied material palette in accordance with Moore’s law, the need for novel digital etch methods to enable the precise removal of thin film materials is of extreme importance.

While there are anisotropic W ALE processing methodologies available, isotropic thermal ALE techniques are required to perform conformal etch in high aspect ratio structures. Indeed, progress toward the isotropic thermal ALE of metallic W has been reported by the groups of George and...

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Accordingly, to enable the rapid development of such processes, it is imperative that a mechanistic understanding of W ALE be established. Herein, we report a first-principles computational study using density functional theory (DFT) to explore an oxidation/chlorination thermal ALE mechanism for W metal. In this study, the nature of the surface oxidation step to produce a WO₃ layer on tungsten is investigated using O₂, O₃, and N₂O as oxidants to uncover potential routes toward self-limiting oxidation of the W surface. Second, WCl₆ and Cl₂ were examined as potential etch reagents to generate volatile WO₂F₂ byproduct. They have also reported results on an oxidation plus WCl₆-based W ALE process in which they sequentially generating a B₂O₃ surface layer, which is then susceptible to self-limiting etching by HF. Parsons and coworkers have recently reported the ALE process of W with sequential use of O₂ plasma or O₃ and WF₆. The oxidizing plasma produces a diffusion-limited WO₃ surface layer, which can be removed by exposure to WF₆ yielding WO₂F₂ as a volatile etch byproduct. 

## 2. COMPUTATIONAL SETUP

All calculations reported in this paper are based on spin-polarized DFT using VASP v5.4. Core electrons are represented by projector augmented wave (PAW) potentials, and valence electrons are treated explicitly by expanding their wave functions in a plane wave basis set with an energy cutoff of 400 eV. The exchange and correlation (XC) contributions are approximated by the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) functional. The total energies and forces of the geometries are converged within 1 × 10⁻⁴ eV Å⁻¹ and -0.02 eV Å⁻¹, respectively. Methfessel–Paxton first-order smearing with 0.1 eV broadening is used for the scf calculations. The effect of dispersion correction on the structure and energies of bulk and surface geometries was found to be insignificant for this system, and thus dispersion corrections are not included (see section S0 of the Supporting Information).

The reported reaction free energies are computed as follows:

\[ \Delta G = \Delta H - T \Delta S + RT \ln(Q) \]  
\[ \Delta H = \Delta E + \Delta ZPE + \Delta W(T) \]  
\[ Q = \prod_{i} P_{\text{products}}^{i} \prod_{j} P_{\text{reactants}}^{j} \]

Here, \( \Delta G \), \( \Delta H \), and \( \Delta S \) correspond to reaction free energy, reaction enthalpy, and reaction entropy, respectively. \( \Delta E \), \( \Delta ZPE \), and \( \Delta W(T) \) refer to the electronic reaction energy at 0 K, zero point energy change, and temperature-dependent enthalpy change, respectively. Q is the reaction quotient used to include reactant and product pressures. A reactant pressure of 0.2 Torr and a product pressure of 0.01 Torr are used for the reported free energy calculations (see section S7 of the Supporting Information for other pressure combinations). Pressure contributions to the free energy are included only for the gas phase species. R and \( \mu \) are the gas constant and stoichiometric coefficient, respectively. The H and S values of the bulk and surface geometries are computed using the Phonopy code, which requires accurate force constants obtained from DFPT calculations in VASP with a strict energy convergence threshold of 1.0 × 10⁻⁸ eV. However, for convenience, the H and S values for gas phase molecules are obtained from the Turbomole package version 6.2 using the PBE XC functional and the def-TZVPP basis set.

W has a BCC crystal structure with a calculated lattice constant of 3.17 Å, which agrees with the experimental value of 3.16 Å. The cohesive energy of W is 9.1 eV/atom, which compares well to the experimental value of 8.9 eV/atom. For the bulk W calculation, a 12 Å × 12 Å Monkhorst-Pack K-point sampling mesh is used and the lattice constant is obtained by simultaneously relaxing the ionic positions, cell shape, and cell volume at a larger plane wave energy cutoff of 550 eV. For the surface calculations, we have chosen the (2 × 3) supercell of a 10.8 Å thick stepped W(3 1 0) surface that has a computed surface energy of 3.77 J/m². The high index high energy W stepped surface was chosen so as to maximize reactivity to incoming reagents as compared to the flat, less reactive low index surfaces. This metal slab consists of six W bilayers with 12 atoms each (72 W atoms in total) with a surface area of 0.955 nm². A vacuum of 19 Å separates the two surfaces of the slab along the surface normal direction. A 3 × 3 × 1 Monkhorst-Pack K-point sampling mesh is used for all surface calculations to account for the supercell size used in this study. Atomistic models of bulk W and W(3 1 0) surface are shown in Figure S1 of the Supporting Information.

Tungsten sites are 8-fold coordinated in the bulk due to the BCC crystal structure. Each bulk W atom has six valence electrons shared between eight neighbors; therefore, three-fourths of an electron is contributed to each metallic W–W bond. In the (2 × 3) supercell of W(3 1 0), there are 12 surface W atoms of which 6 are 4-fold coordinated and the other 6 are 6-fold coordinated. This amounts to 27 unpaired electrons on the surface. Therefore, we adsorbed 14 O atoms (coverage of 14.7 O/nm²) per supercell to the bare surface to represent an oxidized W surface region, which is computationally tractable. The degree of oxidation will depend on processing conditions (section 3.2), but this provides a reasonable model of partially oxidized W for our analysis. We considered different arrangements of O species on the surface and relaxed the geometries (see Figure S2 of the Supporting Information). The most stable WO₅ structure we have found is shown in Figure 1a,b.
the partially oxidized W surface that is present after the first ALE (oxidation) pulse. From Figure 1a,b, we find that the O atoms prefer to adsorb at the bridge and 3-fold sites on the surface. Moreover, the surface W–O bonds would weaken the underlying W–W bonds, which is evident from the out-of-lattice positions of the surface W atoms highlighted in red.

3. RESULTS

3.1. Volatile Products of Interest. The proposed W-etch species, which originate from the surface for this ALE process, have been determined to be either WOCl₄ or WO₂Cl₂ depending on the etch gas stoichiometry. To etch a single atom of W from the surface (Ws) with a single molecule of WCl₆, the incoming WCl₆ molecule must react with the surface to generate a minimum of two volatile W species in the form of WOCl₄ or WO₂Cl₂. In order to maintain proper “book-keeping” of volatile species, it is important to note that the first volatile W species corresponds to the W atom originating from the incoming WCl₆ molecule. Due to the origin of this W atom from the reactant gas, the resulting volatile W species (either WOCl₄ or WO₂Cl₂) is considered a non-Ws etch species (NES), while the second W-containing species would be designated the first-Ws etch species (FES). In the most favorable case, one incoming WCl₆ could react with the surface to form 3 equiv of WO₂Cl₂ thereby effectively etching two surface W atoms. The first molecule of WO₂Cl₂ would be a NES, while the first and second W species that originate from the surface would be considered the first-Ws etch species (FES) and second-Ws etch species (SES), respectively. This nomenclature is used throughout the remainder of this paper. Alternatively, a second mechanism utilizing 2 equiv of WCl₆ to remove one surface W atom resulting in the formation three WOCl₄ species is also considered. The first two W species, which originate from the incoming WCl₆ molecule, would be considered NESs, while the last W species, which originates from the surface, would be a FES.

If we consider Cl₂ as an etch gas, each molecule of Cl₂ has the potential to remove an oxidized surface W atom in the form of WO₂Cl₂ (a FES). Likewise, 2 equiv of Cl₂ could be used to form 1 equiv of WOCl₄ originated from the surface (a FES). A schematic showing the described volatile byproducts is shown in Figure S3 of the Supporting Information. It is important to note that the formation energies for these proposed volatile species were very similar (WOCl₄: −7.1 eV; WO₂Cl₂: −7.3 eV) using bulk W, O₂, and Cl₂ molecules as a reference. However, their formation and desorption energies with respect to a reactive surface differ and will be addressed later in this text. We first study how the oxidizing agents interact with the bare surface to form the WO₃ surface shown in Figure 1a and then examine how WCl₆ and Cl₂ molecules interact with this oxidized W surface.

3.2. Mechanisms in the Oxidation Pulse. In the first ALE pulse, we modify the W surface by oxidizing it with O₂, O₃, and N₂O. N₂O interaction with the bare W surface is the weakest when compared to O₂ and O₃; therefore, the discussion on N₂O–W interaction is moved to section S2 of the Supporting Information. Oxidation of W using O₂ and O₃ has been studied quite extensively, and it is known that bulk oxidation of W in an O₂ atmosphere is appreciable only above 500 °C, which is well above the ALE processing temperature. From the N-E analysis given in section S3 of the Supporting Information, comparing the continuous and self-limiting reaction models of the first ALE pulse, we predicted a minimum (thermodynamic) energy barrier of about 2.3 eV to cause bulk oxidation. We could expect that the predicted thermodynamic barrier to be breached below 800 °C as W oxide, formed on the surface, is reported to become volatile beyond that temperature. Warren et al. found that a 1 h exposure of polycrystalline W to O₂ below 200 °C resulted in the formation of 1.0–1.6 nm of WO₃. Therefore, by keeping the temperature below 200 °C or by controlling the exposure time and partial pressure of the reactants, a thin layer of oxide relevant for ALE can be formed. The temperature needed for the thermal ALE process will also be influenced by the activation energies required in the second ALE pulse.

On the clean W(3 1 0) surface, both O₂ and O₃ molecules dissociate spontaneously on adsorption and form surface W–O bonds as shown in Figure 1a,b by releasing −7.24 and −12.13 eV per adsorbed molecule, respectively. For comparison, the most favorable binding energy of a N₂O molecule is −5.81 eV. O₃ is a stronger oxidant than the O₂ molecule. Since the adsorption geometries and binding sites are similar for both molecules, we will only examine the adsorption of the O₂ molecule in detail. We considered different binding sites for the dissociated O atoms on the W surface as shown in Figure 2a–e. The binding energies and shortest W–O bond distances from these geometries are listed in Table 1. The computed binding energy per O atom in is in the range of −3.30 to −4.47 eV for on-surface adsorption, with the bridge sites being the most favorable followed by the atop, 3-fold, and 4-fold sites. The adsorption at subsurface sites is about 3 eV less favorable than the most favorable bridge site (Figure 2f). Clearly, at this coverage of 2 O/nm², diffusion to subsurface sites is not as favorable as on-surface adsorption. The O atom in the subsurface site is at least 1.9 Å away from the neighboring W atoms. The shortest W–O bond length is found at the atop site followed by the bridge, subsurface, 3-fold, and 4-fold sites. Comparing with the most favorable oxygen-covered surface model shown in Figure 1a, we note that the O atoms are predominantly adsorbed at the bridge sites.

In this section, we saw the various adsorption sites preferred by the dissociated O atoms and that the O₂ molecule indeed dissociates spontaneously. We have prepared the saturated surface models as described in the computational section. Any additional O₂ molecule introduced in the system beyond a...
single O₂ molecule described in this section will indeed dissociate (in an exoergic reaction) until the saturated surface is formed. Thus, the intermediate steps do not need to be discussed.

3.3. Mechanisms in the Chlorination Pulse. The primary mechanism of chlorination of the oxidized W surface by WCl₆ is the dissociation of the molecule and subsequent exchange of Cl ligands from the reagent to the substrate, which requires elevated temperatures. These are complex dynamical processes unlike the simple dissociative adsorption of the reactant molecules in the first pulse. Before investigating the chlorination of the oxidized W surface, we first explored the possibility of uncontrolled etching of W metal by WCl₆ and Cl₂. These results are discussed in detail in section S4 of the Supporting Information. The exposure of WCl₆ and Cl₂ on the W(3 1 0) surface at atop sites, bridge sites, alternate bridge sites, 3-fold sites, 4-fold sites, and subsurface sites are shown in (a), (b), (c), (d), (e), and (f), respectively. The color coding is as follows: W = gray, O = red.

![Figure 2](image)

**Figure 2.** The top and side views of dissociated O₂ molecules on the W(3 1 0) surface at atop sites, bridge sites, alternate bridge sites, 3-fold sites, 4-fold sites, and subsurface sites are shown in (a), (b), (c), (d), (e), and (f), respectively. The color coding is as follows: W = gray, O = red.

### Table 1. Binding Energies and Minimum W–O Bond Distance for O₂ adsorption on the W(3 1 0) Surface

<table>
<thead>
<tr>
<th>geometry</th>
<th>Ebind (eV/O)</th>
<th>d(W–O) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>atop</td>
<td>−3.80</td>
<td>1.7</td>
</tr>
<tr>
<td>bridge</td>
<td>−4.47</td>
<td>1.9</td>
</tr>
<tr>
<td>bridge2</td>
<td>−3.99</td>
<td>1.9</td>
</tr>
<tr>
<td>3-fold</td>
<td>−3.31</td>
<td>2.0</td>
</tr>
<tr>
<td>4-fold</td>
<td>−3.30</td>
<td>2.1</td>
</tr>
<tr>
<td>subsurface</td>
<td>−1.45</td>
<td>1.7 (1.9)</td>
</tr>
</tbody>
</table>

For the subsurface geometry, the distance in parentheses correspond to the O atom in the subsurface site.

of the kinetic energy barrier. Dissociation of the WCl₆ molecule would need elevated temperatures to excite the W–Cl bonds or O-free regions on the surface as WCl₆ readily dissociates on the bare W surface. Experiments suggest that a temperature of at least 200 °C is needed for the ALE process to take place, which means that the WCl₆ molecules would have dissociated at this temperature. A short 2.5 ps duration ab initio molecular dynamics (MD) simulation at 800 K of the WOₓ surface with two physisorbed WCl₆ molecules revealed a spontaneous donation of one of the Cl ligands by each of the reactant molecules to the surface W atoms as shown in Figure 3. A high temperature of 800 K is used to accelerate the MD simulation; otherwise, we would have needed a significantly longer simulation time to observe this reaction step at lower temperatures.

The W atom in the WCl₆ molecule is the donor W atom (Wₐ), while the acceptor W (Wₐ) is one of the oxidized surface W atoms. In the first 300 steps (750 fs) of the simulation, we can identify the high amplitude vibrational mode of the Cl atom from the fluctuations in the interatomic Wₐ–Cl distances (see Figure 3). Moreover, an increase in the Wₐ–Cl distance correlates with a decrease in the Wₐ–Cl distance. This large amplitude motion, a byproduct of the thermal energy contribution, results in the dissociation of one of the Cl ligands from the WCl₆ molecule. After the crossover point at 837 fs (step 335), the dissociated Cl ligand did not attempt to bind back to the Wₐ atom, which is evident from the continuous increase in d(Wₐ–Cl) value beyond 1.25 ps (step 500). The inset graph in Figure 3 shows the distances and single-point energies of the system during the dissociation of WCl₆. We see an energy change of 800 meV right before the dissociation takes place; this includes contribution from the motion of surface atoms as well. The dissociation of the Cl ligand from the second WCl₆ molecule was similar to the above observation.

To compute the entire dissociation pathway, the formation of non-volatile species are considered when WCl₆ is adsorbed either as an intact or dissociated molecule, for which the geometries are shown in Figure 4A–E. While there are many possibilities to arrange an intact and dissociated WCl₆ molecule on the O-covered W surface, it is not practical to study them all; therefore, we have considered these five minimum geometries as a representative for further discussion. In Figure 4, geometry A shows a weak interaction between the WCl₆ molecule and the O-covered W surface with a binding energy of just −0.09 eV. Geometry B shows the state where the weakly adsorbed WCl₆ dissociates and a Cl ligand is adsorbed to a surface W atom. This reaction is not spontaneous and costs 0.48 eV. The potential energy surface cut along the pathway, obtained by a linear interpolation of the position of the dissociated Cl ligand from geometry A to B, is computed, and the computed dissociation barrier is 0.52 eV (graph and geometries in Figure S9 of the Supporting Information). The reverse barrier for the reformation of WCl₆ is just 0.04 eV. However, this reaction is hindered by the diffusion of the WCl₃ fragment into the vacuum immediately after the dissociation. It is possible that all impinged WCl₆ molecules follow this process and chlorinates the WOₓ surface without depositing any W as WCl₄. However, the WCl₃ fragment in the gas phase can further adsorb on the surface by forming W–O bonds as shown in geometry C (WCl₃ adsorbed), which is energetically favorable and releases −1.32 eV of energy in comparison to geometry B. Dissociation of a Cl ligand from the adsorbed
WCl₅ fragment in geometry C to form geometry D has an energy cost of 1.56 eV, suggesting that further dissociation of Cl ligands from surface-adsorbed WCl₅ has a large energy penalty. Dissociation of surface-bound WCl₅ is unfavorable at 0 K due to enthalpic loss, which will be compensated by entropic gain at elevated temperatures due to the formation of the volatile species (WOCl₄). Another possibility for the WCl₅ fragment in geometry B is to form geometry E by donating another Cl ligand in the gas phase to the surface and adsorb as WCl₄ by forming a W⁻O bond (WCl₄ hop). This results in the formation of WOCl₄, one of the proposed volatile species, which spontaneously desorbs from the surface, as shown in geometry E. Once again, this step will see an entropic gain at elevated temperatures and compensate the enthalpic loss reported at 0 K. Only geometries A and C have favorable (negative) binding energies at 0 K.

Beginning from the most favorable non-volatile adsorption geometry C, step-by-step desorption of the proposed volatile etch products and their corresponding energetics are investigated as shown in Figure 5. Three cases in which the sequential removal of 1 WOCl₄ + 1 WO₂Cl₂, 1 WO₂Cl₂ + 1 WOCl₄, and 3 WO₂Cl₂ are considered. Note that the first volatile product removed in all three cases is the NES followed by FES and SES as discussed earlier. In the first case, WOCl₄ was removed as the NES, with a desorption energy of 0.44 eV. Due to entropic gain, this step is favorable (∼1.73 eV gain) at 500 K. This however does not count toward etching of the Cl ligands from surface-adsorbed WCl₅ has a large energy penalty. Dissociation of surface-bound WCl₅ is unfavorable at 0 K due to enthalpic loss, which will be compensated by entropic gain at elevated temperatures due to the formation of the volatile species (WOCl₄). Another possibility for the WCl₅ fragment in geometry B is to form geometry E by donating another Cl ligand in the gas phase to the surface and adsorb as WCl₄ by forming a W⁻O bond (WCl₄ hop). This results in the formation of WOCl₄, one of the proposed volatile species, which spontaneously desorbs from the surface, as shown in geometry E. Once again, this step will see an entropic gain at elevated temperatures and compensate the enthalpic loss reported at 0 K. Only geometries A and C have favorable (negative) binding energies at 0 K.

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substrate since the W atom removed is not a surface atom. Following this step, WOCl₄ is removed as the FES with an additional desorption energy of 2.57 eV (which is also not favorable at 500 K). In the second case, WO₂Cl₂ is removed first as the NES with an energy cost of 0.57 eV, which is 0.13 eV more than WOCl₄ in the first pathway. This is because a second W−O bond must be broken in forming WO₂Cl₂. The subsequent removal of WOCl₄ in this sequence costs 2.72 eV of energy. We note that WOCl₄ offers more entropy than WO₂Cl₂ due to the presence of an additional ligand, and it is evident from the reduced free energy gain in the first step (−1.37 eV for WO₂Cl₂ against −1.73 eV for WOCl₄) and reduced free energy loss in the second step (0.54 eV for WOCl₄ against 0.64 eV for WO₂Cl₂) when compared with the previous case. In these two cases, the removal of the FES is not favorable even at 500 K. However, the cumulative enthalpic gain in the earlier steps of the ALE cycle could offset this energy cost.

In the third case, three WO₂Cl₂ molecules were removed sequentially. While the removal of the NES costs 0.57 eV, the removal of the FES and SES becomes increasingly expensive with energy costs of 1.00 and 4.42 eV, respectively. In contrast to the first two cases, the removal of the FES in this case is favorable at 500 K (−0.93 eV); however, the removal of the SES is not. This is due to the fact that a considerable number of surface W−O and W−W bonds have to be broken to remove the second WO₂Cl₂ species. Similarly, from the minimum geometry E, the removal of the pre-formed non-W, etch WOCl₄ is favorable by −0.29 eV. Further removal of the etch product WOCl₂ costs an energy of 1.0 eV, but this step is entropically favorable at 500 K in contrast to the first case from geometry C. The free energy values for other reactant and product pressures for comparison is given in section S7 of the Supporting Information. It is to be noted that the influence of the reactant pressure to the free energy is very small compared to the contributions from enthalpy and entropy in this case.

From the above analysis, we find that each WCl₆ molecule is capable of removing up to two surface W atoms and six surface O atoms in the best case scenario (3 WO₂Cl₂). However, the removal of the W atoms from the surface costs anywhere between 1.00 and 4.42 eV. We also find that the removal of WOCl₄ as a non-W, etch product costs less energy when compared to WO₂Cl₂ since the former removed only one surface-bound O atom whereas the latter removes two, which costs more energy. This is further supported by the observation that, whenever a WOCl₄ species is formed on the surface, it readily desorbs from the surface. In contrast, WO₂Cl₂ is bound to the surface primarily as a result of the strong W−W and W−O bonds. Therefore, WO₂Cl₂ should become volatile only at elevated temperatures.

To consider other combinations of etch products, 2 WCl₆ adsorption on the O-covered W surface is studied as shown in Figure 6. Similar to the low coverage case, the interaction between WCl₆ and the substrate was weak with a binding energy of just −0.07 eV/WCl₆ (geometry A). Dissociation of the adsorbed WCl₆ molecules by donating one Cl atom to the surface (geometry B) costs about 0.27 eV/WCl₆. Keeping geometry B as the starting point, we computed the desorption energies for the removal of three consecutive WOCl₄ species. The removal of the first two volatile species (NESs) is exergic, while the removal of the third WOCl₄ (FEP) has a cost of 1.08 eV. The removal of the above three volatile products was favorable at 500 K. In another desorption sequence, we studied the desorption of two consecutive WCl₆ as the NES followed by two WO₂Cl₂ as the FES and SES. While the removal of the first two WOCl₄ species was essentially the same as in the previous case, the subsequent removal of the first WO₂Cl₂ species costs less energy compared to the energy cost for removal of WOCl₄ in the other sequence. However, the removal of the second surface W atom in the form of WO₂Cl₂ has a huge energy penalty of 4.7 eV. We find that the removal of a surface atom as WO₂Cl₂ is not more energetically favorable than its removal as WO₃Cl₂, which is understandable as more surface W−O/W−W bonds have to be broken to form the former than the latter in this particular.

<table>
<thead>
<tr>
<th>Desorption events</th>
<th>NES</th>
<th>FES</th>
<th>SES</th>
</tr>
</thead>
<tbody>
<tr>
<td>0: WCl₆ adsorbed</td>
<td>-0.07 W₆</td>
<td>1.00 W₆</td>
<td>4.42 W₆</td>
</tr>
<tr>
<td>2: WCl₆</td>
<td>-1.37 W₆</td>
<td>-0.93 W₆</td>
<td>2.48 W₆</td>
</tr>
<tr>
<td>2: WCl₆</td>
<td>0.57</td>
<td>2.72</td>
<td></td>
</tr>
<tr>
<td>2: WCl₆</td>
<td>-1.37</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>2: WCl₆</td>
<td>0.44</td>
<td>2.57</td>
<td></td>
</tr>
<tr>
<td>2: WCl₆</td>
<td>-1.73</td>
<td>0.64</td>
<td></td>
</tr>
<tr>
<td>2: WCl₆</td>
<td>-2.46</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>2: WCl₆</td>
<td>-0.29</td>
<td>-0.92</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5. Energy requirements for the removal of volatile species from geometry C and E from Figure 4. The values in red indicate a moderate energy cost, and the values in green indicate a gain in energy. The values above the arrow are the desorption energies of the respective volatile species, while the values below are the free energy change of desorption at 500 K. The desorbed molecules are either WOCl₄ or WO₂Cl₂.

<table>
<thead>
<tr>
<th>Desorption events</th>
<th>NES1</th>
<th>NES2</th>
<th>FES</th>
<th>SES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: WCl₆</td>
<td>-0.53</td>
<td>-0.53</td>
<td>1.08</td>
<td></td>
</tr>
<tr>
<td>1: WCl₆</td>
<td>-2.70</td>
<td>-2.51</td>
<td>-1.08</td>
<td></td>
</tr>
<tr>
<td>1: WCl₆</td>
<td>-0.53</td>
<td>-0.35</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>1: WCl₆</td>
<td>-2.70</td>
<td>-2.51</td>
<td>-1.45</td>
<td></td>
</tr>
<tr>
<td>1: WCl₆</td>
<td>-0.54</td>
<td>2.80</td>
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Figure 6. Minimum energy geometries showing the non-volatile adsorption of 2 WCl₆ on the O-covered W surface and energies needed to remove volatile species from them. The values in red indicate energy loss, and the values in green indicate energy gain. The values above the arrow are the desorption energies of the respective volatile species, while the values below are the free energy change of desorption at 500 K.
case. On the other hand, it is more favorable to form WOCl$_4$ as a NES from the incoming WCl$_6$ molecule when compared to WO$_2$Cl$_2$.

Now, let us look at the chlorination pulse when Cl$_2$ is used as the gas phase reactant. Similar to WCl$_6$, Cl$_2$ did not adsorb strongly via dissociation at the O-rich region of the WO$_x$ surface. A binding energy of just $-0.05$ eV per Cl$_2$ molecule is obtained. A short MD simulation at 800 K also failed to capture Cl$_2$ dissociation as the Cl$_2$ molecule simply diffused away from the surface due to the repulsion between the Cl and surface O atoms. Therefore, we studied the dissociative adsorption of 1 and 2 Cl$_2$ on the model WO$_x$ surface, which released an energy of $-3.11$ to $-3.92$ eV per adsorbed Cl$_2$. The corresponding geometries are schematically presented in section S8 of the Supporting Information. From the above structures, desorption energies of volatile species such as WO$_2$Cl$_2$ and WOCl$_4$ are computed to be 1.33 and 0.73 eV, respectively. It is to be noted that there is no NES when Cl$_2$ is used in the chlorination pulse. Also, as mentioned earlier in Section 3.1, each Cl$_2$ molecule is capable of forming, at most, one etch product (WO$_2$Cl$_2$ as the FES), whereas two Cl$_2$ molecules are needed to form one WOCl$_4$ (as the FES) or two WO$_2$Cl$_2$ (as the FES and SES). On the bare W surface, Cl$_2$ dissociates spontaneously at low temperatures (discussed in detail in section S4 of the Supporting Information). Homolytic dissociation of Cl$_2$ is required on the WO$_x$ surface so that volatile species can be formed. Dissociation of Cl$_2$ in vacuum requires 3.1 eV, while the dissociation of one W$-$Cl bond from the WCl$_6$ molecule in vacuum required a slightly lower 2.5 eV. Based on the above, WCl$_6$ may dissociate at lower temperatures when compared to Cl$_2$. Therefore, in the next section, we will discuss the full ALE cycle with WCl$_6$ as the second pulse chemical.

### 3.4. The Full Atomic Layer Etch Cycle

In this section, we discuss the full cycle of the W ALE process, with O$_2$, O$_3$, and N$_2$O as the first pulse chemical and WCl$_6$ as the second pulse chemical, which is summarized in Figure 7A. Steps 1, 2, 3, and 4 correspond to pulse-1, purge-1, pulse-2, and purge-2 of the W ALE cycle, respectively. Step 5 is also the step 1 of the second and subsequent ALE cycles, whereas steps 2, 3, and 4 are common for all ALE cycles. The first ALE pulse is the adsorption of the oxidizing agents (O$_2$, O$_3$, and N$_2$O). In the oxidation step, step 1 of the first ALE cycle, energy is gained by the dissociative adsorption of the reactant molecules on the bare W surface. We will show later that subsequent ALE cycles do not start with a bare W surface but rather a WO$_x$Cl$_y$ surface. We show in Table 2 and section S3 of the Supporting Information that this step realizes a significant enthalpy gain by the formation of stable W$-$O bonds, but the associated entropic loss was comparatively too small to make the reaction unfavorable at ALE relevant temperatures.

An energy of $-4.31$ to $-4.80$ eV ($-3.61$ to $-4.63$ eV at 500 K), depending on the first pulse reactant used, is gained per surface W atom in the supercell (W$_s$, note that there are 12 W$_s$ in the supercell) in this step. This amounts to an energy of $-3.69$ to $-4.11$ eV released per O atom adsorbed. In step 2, unreacted reactant molecules are purged from the etch chamber along with any byproducts formed.

In step 3, the dissociative adsorption of WCl$_6$ is either mildly favorable energetically ($-0.08$ eV/W$_s$) or costs energy ($0.12$ eV/W$_s$). Therefore, in the next section, we will discuss the full ALE cycle with WCl$_6$ as the second pulse chemical.

![Figure 7. Panel (A) shows a schematic representation of an idealized W ALE cycle. The energies of the individual steps are listed in Table 2. Atom color coding is as follows: W = gray, O = red, and Cl = green. Step 1 depicts the initial functionalization of the surface with the desired oxidant. Step 2 describes the purging of the excess oxidant from the reaction chamber. Step 3 describes the introduction of WCl$_6$ which exhibits no spontaneous dissociation until elevated temperatures. Step 4 depicts the liberation of volatile WOCl$_4$ species as the most likely etch species. Step 5 in an idealized system results in the repassivation of the surface leading into the next cycle and is thus labeled as equivalent to step 1. Additional passivated surface post etch is shown in panel (B). WCl$_6$ terminated surface is discussed in detail in Figure 8.](https://dx.doi.org/10.1021/acsami.0c06628)
Table 2. Energy Requirements (Ranges with Most Favorable (MF) and Least Favorable (LF) Values in eV) for the Individual Steps of the ALE Cycle in Figure 7

<table>
<thead>
<tr>
<th>step</th>
<th>ΔE (eV)</th>
<th>ΔG (eV) 500 K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MF</td>
<td>LF</td>
</tr>
<tr>
<td></td>
<td>MF</td>
<td>LF</td>
</tr>
<tr>
<td>O₂/O₃/N₂O pulse</td>
<td>–4.80</td>
<td>–4.31</td>
</tr>
<tr>
<td>purge 1</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>WCl₆ pulse</td>
<td>–0.08</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>–4.88</td>
<td>–4.19</td>
</tr>
<tr>
<td>purge 2</td>
<td>–0.53</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>0.48</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td>4.42</td>
<td>4.74</td>
</tr>
</tbody>
</table>

“Here, W̄₁ refers to a surface W atom. NES, FES, and SES are acronyms for non-W̄₁ etch, first-W̄₁ etch, and second-W̄₁ etch species, respectively. The values in bold refer to the cumulative values combining oxidation pulse and chlorination pulse. For the free energy values at 500 K, the contributions from surface models are not included as they were estimated to be less than 4% of the total value.

(continued)
whereby dissociated O₂ molecules are adsorbed on the Cl-covered W surface (Figure 8),. In Figure 8b, the resulting O atoms are adsorbed close to the surface W atoms, which on relaxation resulted in the spontaneous formation of surface-bound WCl₆Cl₄ species with a release of −2.4 eV per adsorbed O atom. In the second configuration (Figure 8c), oxygen atoms are adsorbed close to the Cl atoms, and upon relaxation, we observe the spontaneous formation and desorption of oxychloride species such as ClO₂, Cl₂O₂, and Cl₃O₂, with a gain of −1.0 eV/O. This suggests that the incoming O₂ molecule in the second ALE cycle must first dissociate before adsorbing at the fully chlorinated surface in order to react with it. As mentioned earlier, this pre-dissociation of the O₂ molecules is not needed when the Cl ligands are sparsely distributed on the surface.

4. CONCLUSIONS

A first-principles investigation of a thermal atomic layer etch process for metallic tungsten using sequential oxidation and chlorination is presented. O₂, O₃, and N₂O were examined as the oxidizing agents to modify the oxidation state of the surface W atoms. WCl₆ and Cl₂ were examined as ligand exchange agents for the material removal pulse. The reactant molecules chosen for both ALE pulses meet the requirement of being stable in the gas phase at the ALE operating temperature. Runaway oxidation of W is possible when O₂ and O₃ are used in the first ALE pulse. However, a thin layer of WOₓ can be obtained by carefully controlling the reactant pressure, temperature, and exposure time. The most important aspect of the ALE process is the self-limiting nature of the reactions taking place in the two pulses. Qualitative predictions based on thermochemical analysis showed that bulk oxidation was hindered by thermodynamic barriers at ALE relevant temperatures and pressures. Similarly, spontaneous etching of W by WCl₆ and Cl₂ was predicted to be unfavorable, even though these molecules spontaneously react with the bare W surface.

The mechanisms of the dissociative adsorption of the oxidizing agents on the bare W surface were reported. Exposure to O₂, O₃, and N₂O resulted in an O-covered surface with ozone being the most reactive chemical for the first pulse followed by O₂ and N₂O. To keep the computational effort tractable, we considered a monolayer oxidized surface model of W at the end of the first half ALE cycle. However, WCl₆ molecules interacted weakly with the oxidized W surface due to net repulsion between the O and Cl atoms and also because of the kinetic barriers inhibiting the dissociation of WCl₆ molecule. Thermal energy is required to dissociate the WCl₆ molecule so that it can donate its Cl ligands to the surface leading to the formation of the target volatile species, primarily WOCI and WO₂Cl₂. The incoming WCl₆ molecule can form WOCI as a non-W₇ etch species by exchanging two Cl ligands for one O atom from the surface. This also results in the formation of a WO₂Cl₂ species on the surface. The desorption of WO₂Cl₂ has a relatively higher energy cost as compared to WOCI due to the relatively high coordination of the W atom in surface-bound WO₂Cl₂. The other possibility for the incoming WCl₆ molecule is to dissociate completely by donating all of the Cl ligands to the surface and form three WO₂Cl₂ molecules as volatile species. Therefore, each WCl₆ molecule is capable of removing up to two surface W atoms with a maximum energy cost of 4.42 eV. The desorption of the first-W₇ etch product costs between 0.48 and 2.72 eV, which is thermodynamically favorable in the overall energy cycle, whereas the desorption of the second etch product costs almost 5 eV and is unfavorable.

Due to the favorable reaction of WCl₆ and Cl₂ on the bare W surface, it will be covered with O and Cl ligands at the end of the first ALE pulse. In the second ALE cycle, the oxidizing agents must remove the Cl ligands first, either by forming volatile W oxychlorides or stable oxychloride chains, before accessing the surface W atoms, which might slow down the etch process. Computational investigations of such ALE processes provide the required understanding of the mechanism of etch reactions. Such understanding is vital to the design of new and robust ALE processes in the future.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c06628.

Atomic models of W bulk and surface, schematics of second ALE pulse, mechanism of N₂O pulse, Natarajan–Elliott “N-E” analysis of the oxidation pulse, reaction of WCl₆ and Cl₂ on the bare W surface, dissociation pathway of WCl₆, description of thermal ALE of metals, influence of reactant and product pressures, and Cl₂ in material removal pulse (PDF)

AUTHOR INFORMATION

Corresponding Author

Suresh Kondati Natarajan — University College Cork, Tyndall National Institute, Cork T12 RSCF, Ireland; Department of Electrical Engineering and Automation, Aalto University, Espoo 02150, Finland; orcid.org/0000-0002-7018-5253; Email: suresh0807@gmail.com

Authors

Michael Nolan — University College Cork, Tyndall National Institute, Cork T12 RSCF, Ireland; Nanotechnology and Integrated Bioengineering Centre, Ulster University, Co Antrim BT37 OQB, Northern Ireland; orcid.org/0000-0002-5224-8580

Patrick Theofanis — Intel Corporation, Hillsboro, Oregon 97124, United States

Charles Mokhtarzadeh — Intel Corporation, Hillsboro, Oregon 97124, United States

Scott B. Clendenning — Intel Corporation, Hillsboro, Oregon 97124, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c06628

Notes

The authors declare no competing financial interest.

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REFERENCES

Sn(acac)2 and HF.

J. Phys. Chem. C
Al2O3 Atomic Layer Etching Using Sequential Reactions with Hydrogen Fluoride.

ACS Nano
Sequential Exposures Of Trimethylaluminum and Hydrogen Fluoride.
Sequential, Self-limiting Hydrogen Fluoride and Sn(acac)2 Reactions
Neutral Beam.
Sequential, Self-limiting Thermal Reactions.

J. Vac. Sci. Technol., A

ACS Applied Materials & Interfaces
Sn(acac)2 and HF.
and Enhancement by H2 and Ar Plasmas.

ACS Appl. Mater. Interfaces
(11) Lee, Y.; George, S. M. Thermal Atomic Layer Etching of Crystalline GaN
of ZnO by a
(25) Xie, W.; Lemaire, P.; Parsons, G. N. Self-limiting Thermal Atomic Layer Etching of Tungsten Metal Using O2 Oxidation and WCl6 or WF6: Role of Halogen Species in Temperature Dependence of ALE Reaction Rate. AVS ALE Workshop; 2018, Incheon, South Korea.
(26) Xie, W.; Parsons, G. N. Thermal Atomic Layer Etching of Metallic Tungsten Via Oxidation and Etch Reaction Mechanism Using O2 or O3 for Oxidation and WCl6 as the Chlorinating Etchant. J. Vac. Sci. Technol., A 2020, 38, No. 022605.