



Article First-Principles Molecular Dynamics Simulations on Water–Solid Interface Behavior of H₂O-Based Atomic Layer Deposition of Zirconium Dioxide

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Abstract: As an important inorganic material, zirconium dioxide (ZrO_2) has a wide range of applications in the fields of microelectronics, coating, catalysis and energy. Due to its high dielectric constant and thermodynamic stability, ZrO_2 can be used as dielectric material to replace traditional silicon dioxide. Currently, ZrO_2 dielectric films can be prepared by atomic layer deposition (ALD) using water and zirconium precursors, namely H₂O-based ALD. Through density functional theory (DFT) calculations and first-principles molecular dynamics (FPMD) simulations, the adsorption and dissociation of water molecule on the ZrO_2 surface and the water–solid interface reaction were investigated. The results showed that the ZrO_2 (111) surface has four Lewis acid active sites with different coordination environments for the adsorption and dissociation of water. The Zr atom on the surface can interacted with the O atom of the water molecule via the *p* orbital of the O atom and the *d* orbital of the Zr atom. The water molecules could be dissociated via the water–solid interface reaction on the ZrO₂ surface could also provide a reference for the water–solid interface reaction on the ZrO₂ surface could also provide a reference for the water–solid interface reaction of metal oxides, such as H₂O-based ALD.

Keywords: zirconium dioxide (ZrO₂); H₂O-based atomic layer deposition (H₂O-based ALD); watersolid interface reaction; first-principles molecular dynamics (FPMD); density functional theory (DFT)

1. Introduction

Zirconium dioxide (ZrO₂) is an important inorganic material and has wide applications in the fields of microelectronics, coating, catalysis, energy storage and conversion [1–6]. With the further scaling-down of metal-oxide semiconductor field-effect transistor (MOS-FET) devices, the traditional dielectric material, silicon dioxide (SiO₂), fails to overcome the quantum mechanical tunneling effect in the devices [7–13]. Due to its high dielectric constant and thermodynamic stability, ZrO₂ has been used as the dielectric material to replace SiO₂. Currently, ZrO₂ films can be prepared by physical vapor deposition (PVD), chemical vapor deposition (CVD) and atomic layer deposition (ALD) methods. Among these techniques, ALD has an obvious advantage for the gate dielectric ultrathin film for the nanodevices. ALD can accurately control the composition and thickness of the deposited thin films at the atomic level by alternately pumping different precursors into the reactor. It can utilize the self-limiting and self-saturation features of surface reactions, which result in the advantages of excellent three-dimensional conformity, large-area uniformity and precise thickness control of thin films [14–18]. Usually, water can be used as an oxygen source for the ALD preparation of metal oxides, such as Al₂O₃, TiO₂, ZrO₂ and HfO₂.



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Thus, the water–solid interface is an important scientific issue for H₂O-based ALD of metal oxides. Meanwhile, the water–solid interface also performs very important roles in various fields of nature including microelectronics, coating and heterogeneous catalysis [19–22].

 ZrO_2 has three crystalline phases, namely, common monoclinic, tetragonal and cubic crystals. The adsorption behavior of water molecules on the surface of ZrO₂, such as cubic ZrO_2 (111) and (110) and monoclinic ZrO_2 (001), (101) and (111), have been studied [23–30]. For example, Korhonen et al. studied the adsorption of water on the most stable (101) and (111) surfaces of monoclinic ZrO₂ using density functional theory (DFT) and infrared spectroscopy [26,27]. Xia et al. examined the hydration of the m-ZrO₂ (111) surface using ab initio molecular dynamics simulations [29]. By obtaining the phase diagrams of surface dehydration, the representative partially hydrated m- ZrO_2 (111) surfaces at various temperatures are illustrated. The Fourier transform infrared (FTIR) spectroscopy has demonstrated that the m-ZrO₂ surfaces have amounts of acidic and basic hydroxyl groups and undissociated coordinated water molecules [30]. Herein, we focused on the adsorption and dissociation of water molecules on the relatively stable surface of monoclinic ZrO₂ (111) and its water-solid interface reactions using DFT calculations and first-principles molecular dynamics (FPMD) simulations. The structure and density of states (DOS) before and after adsorption and dissociation of water are also investigated. The results show that the Zr atom of the ZrO_2 (111) surface is the active site for the adsorption and dissociation of water. The water molecules close to the surface will be strongly adsorbed on the substrate and form Zr–O bonding sites. Some water molecules will be directly dissociated and form O-H bonds with the O atoms on the substrate surface. The dissociation of water can also occur via a proton exchange reaction between two water molecules on the surface of the monoclinic ZrO₂ (111) surface. These modeling and insights into the water-solid interface reaction of ZrO₂ via FPMD simulations at the atomic level can provide theoretical references for water-solid interface studies of metal oxides, such as H₂O-based ALD.

2. Computational Details

First, the monoclinic ZrO₂ crystal (space group $P_{21/c}$) was optimized. The optimized lattice parameters are 5.16, 5.23 and 5.35 Å, respectively, which are in accordance with the experimental values of 5.15, 5.21 and 5.31 Å [31]. The average length of the Zr–O bond is 2.295 Å. To model the surface, a monoclinic ZrO₂ (111) (1 × 2) surface with 13.37 × 7.40 Å² was adopted. The model includes two, three, four and five layers of ZrO₂. For the structural optimization, the atoms of the lowest layer of the surface were fixed. To ensure that there is enough space to adsorb water molecules and avoid the influence between two interfaces, the vacuum between the two surfaces was set to 20 Å. For the FPMD simulations, three layers of O–Zr–O including 72 atoms were used. At the same time, 55 water molecules were placed in the 20 Å vacuum.

All geometric optimizations were performed using DFT calculations based on the generalized gradient approximation with the Perdew–Burke–Ernzerhof functional and implemented in the Vienna Ab initio Simulation Package (VASP 6.2) [32]. The valence electronic states were expanded based on plane waves with the core–valence interaction represented using the projector augmented plane wave approach [33,34]. An energy cutoff of 520 eV was used. A Γ -centered k-mesh of 7 × 6 × 6 was used for the calculations of the crystal. A Γ -centered k-mesh of 2 × 4 × 1 was used for the calculations of the surface. The convergence criteria for total energies and the forces for ionic relaxation were 1 × 10⁻⁵ eV and 0.02 eV/Å, respectively. For the FPMD simulations, the *NVT* ensemble was used. The temperature was controlled at 373 K using a Nose-Hoover thermostat. The time step was set to 1.0 fs. The total time of the FPMD simulation was 15 ps.

3. Results and Discussion

3.1. Surface Model

Surface model tests were performed using two, three and four layers of ZrO_2 surface, shown in Figure 1. The water molecule was adsorbed on the same site of the ZrO_2 surface

models. The structural parameters and the adsorption energy are shown in Table 1. Here, the adsorption energy can be defined as:

$$E_{ads} = E_{(substrate + adsorbate)} - E_{substrate} - E_{adsorbate}$$
(1)

where $E_{(substrate + adsorbate)}$, $E_{substrate}$ and $E_{adsorbate}$ represent the energies of the system, surface and adsorbate, respectively. The results show that there is almost no difference in the adsorption configuration of the water molecule on the surface models of two, three and four layers. The three adsorption energies are about -18.5 kcal/mol. Due to Zr atoms on the surface are strong Lewis acid sites, water can be strongly adsorbed on the ZrO₂ surface, indicating that this reaction is driven by strong adsorption of adsorbates at strong Lewis acid sites. Meanwhile, all of this indicates that after the surface model reaches a certain thickness, the increase in the substrate thickness has little effect on the configuration and adsorption energy of water molecules on the surface. Therefore, to balance the computational accuracy and cost, the three-layer model of the ZrO₂ surface was adopted for the following calculations.



Figure 1. Structure of a water molecule adsorbed on two-layer (**a**), three-layer (**b**) and four-layer (**c**) models of the monoclinic ZrO₂ (111) surface.

Table 1. Structural parameters and adsorption energies of a water molecule on different models of the ZrO_2 surface.

Layer	d _{O-Zr} /(Å)	$d_{\rm O-H}/({\rm \AA})$	∠HOH/(°)	E _{ads} /(kcal/mol)
2	2.418	0.976/0.994	103.6	-18.3
3	2.404	0.976/0.995	103.6	-18.5
4	2.402	0.977/0.993	103.8	-18.7

3.2. Adsorption and Dissociation of a Water Molecule on the ZrO₂ (111) Surface

As shown in Figure 2, Zr atoms of monoclinic ZrO_2 bulk have seven-fold coordination with O atoms and O atoms have three- or four-fold coordination with Zr atoms. Due to the difference in the relative spatial positions of O atoms coordinated to Zr atoms, there are four nonequivalent Zr atoms with six-fold coordination on the surface of monoclinic ZrO₂ (111). In other words, there are four Lewis acid active sites of surface Zr atoms with different coordination environments on the monoclinic ZrO₂ (111) surface, labeled **A**, **B**, **C** and **D**, respectively. Considering the four orientations of a water molecule at a site, 16 initial structures of a water molecule adsorbed on the surface were investigated. The most stable adsorption structures at the four sites are shown in Figure 3. The corresponding adsorption energies were -20.8, -18.6, -19.5 and -34.0 kcal/mol, respectively.



Figure 2. Four surface Zr atoms (**A**, **B**, **C** and **D**) with different coordination environments on the monoclinic ZrO_2 (111) surface.



Figure 3. Stable adsorption structures of a water molecule at **A**, **B**, **C** and **D** sites on the monoclinic ZrO₂ (111) surface and the corresponding dissociation structures.

Table 2 lists the bond lengths and bond angles of the four stable adsorption structures. At site **A**, the distances between O and H in the water molecule after adsorption are 0.979 and 1.004 Å, and \angle HOH is about 104.4°, whereas the bond length of H–O in the isolated water molecule is 0.97 Å and \angle HOH is about 103.6°. The distance between the Zr atom at site **A** and the O atom in the water molecule is 2.364 Å. There is an interaction between the Zr atom on the surface and the O atom in the water molecule. Similar trends were observed in the variation of structural parameters at the **B**, **C** and **D**. In these adsorption structures, the structure of the water molecule is distorted in value by about 5%. The distances between the Zr atom on the surface and the or the water molecules are all about 2.4 Å. All of these indicate that there are strong interactions between the Zr atoms on the surface and the O atoms in the water molecules are all about 2.4 Å.

Site	$d_{\rm O-Zr}/({\rm \AA})$	$d_{\rm O-H}/({\rm \AA})$	∠HOH/(°)	E _{ads} /(kcal/mol)
Α	2.364	0.979/1.004	104.4	-20.8
В	2.394	0.974/0.998	107.8	-18.6
С	2.354	0.977/1.000	106.4	-19.5
D	2.234	0.974/1.067	107.9	-34.0

Table 2. Structural parameters of water adsorption on ZrO₂ surfaces.

Based on the four most stable adsorption structures, the dissociation states of the water molecule on the ZrO_2 surface were also investigated. As shown in Figure 3, the water molecule can be dissociated into a H atom and the hydroxyl group, where the hydroxyl group is adsorbed on the Zr atom on the surface and the H atom interacts with the O atom on the surface to form a new hydroxyl group. Table 3 lists the bond lengths and bond angles of the dissociated structures. At the **A** site, after the dissociation of the water molecule, the distances of O and H in the water molecule are 0.972 and 1.642 Å, and the ∠HOH is about 109.9°. The distance between the O atom of the water molecule and the Zr atom on the surface decreases from 2.364 Å to 2.080 Å. Similarly, at the **B** (0.969/1.691 Å and 136.5°, 2.085 Å), **C** (0.973/1.774 Å and 106.7°, 2.073 Å) and **D** (0.972/1.465 Å and 110.8°, 2.091 Å) sites, the water molecules are dissociated. The O atom in the water molecule and the Zr atom on the Zr atom on the surface are closer together. The distances between Zr and O atoms are below 2.1 Å. All these indicate that the water molecule is dissociated on the ZrO₂ surface and a new Zr–O bond is formed.

Table 3. Structural parameters and related energies of water dissociation on ZrO₂ surfaces.

Site	$d_{\rm O-Zr}/({\rm \AA})$	$d_{\rm O-H}/({\rm \AA})$	∠HOH/(°)	E _{ads} /(kcal/mol)
Α	2.080	0.972/1.642	109.9	-19.3
В	2.085	0.969/1.691	136.5	-16.5
С	2.073	0.973/1.774	106.7	-12.3
D	2.091	0.972/1.465	110.8	-33.9

For comparison, it can be seen that the adsorption energies of the water molecule at the four sites are -20.8, -18.6, -19.5 and -34.0 kcal/mol, respectively. The energies of the dissociated structures of the water molecules are -19.3, -16.5, -12.3 and -33.9 kcal/mol, respectively. These indicate that the adsorption energy and stability of the adsorbed structure are almost the same as that of the dissociated structure at the four sites. Among them, the energy of the dissociation structure at the **C** site is higher by 6.8 kcal/mol than that of the adsorption structure. This is because the different coordination environments of Zr atoms on the surface affect the adsorption and dissociation of small molecules. At the **D** site, the adsorption energy of water molecules is the largest, indicating that the adsorption structure at the **D** site is the most stable. The bonding characteristics between the water molecule and Zr atom at the **D** site on the substrate were further analyzed. The changes in the projected DOS of adsorbed water and dissociation of a water molecule on the **D**

site are shown in Figure 4. The adsorption of a water molecule on the surface of ZrO_2 (111) is mainly through the interaction between the O atom in the water molecule and the Zr atom on the surface. The highest occupied molecular orbital of the water molecule is mainly contributed by the 2p orbital of the O atom and the lowest unoccupied molecular orbital of the O atom is mainly contributed by the 2s orbital of the O atom. The electrons of the *d* orbitals of Zr atoms on the surface fill the nonbonding orbital of the O atom. From Figure 4, it can be seen that the DOS of the water molecule is shifted from lower to higher energy levels when the adsorbed state changes to the dissociated state. These are also in accordance with the results of the water molecule gets more charge in the adsorbed state than in the dissociated adsorbed state. Moreover, the peak of the Zr atom at the Fermi energy level becomes lower in the dissociated state, indicating that the electrons are transferred from the surface to the water molecule.



Figure 4. Density of states (DOS) of H₂O adsorbed on ZrO₂ (111) surfaces and the corresponding dissociative state.

3.3. The Water–Solid Interface Reaction of ZrO₂

To further investigate the adsorption and dissociation behaviors of a large number of water molecules on the ZrO_2 surface, FPMD simulations of the water–solid interface of ZrO_2 were conducted at 373 K. Figure 5 shows the three-layer model structure of the water–solid interface of ZrO_2 , in which 55 water molecules are added into the vacuum slab as the explicit solvent corresponding to the density (1 g/mL) of the water.

To understand the distribution and movement rules of the particles on the surface, the radial distribution functions (RDFs) and their integrated RDFs for H and O in water molecules and for the Zr atom on the ZrO₂ surface were calculated. The RDF g(*r*) is the distribution probability of a given particle α over a particle β when the distance is *r*. As shown in Figure 6, the first peak in g(*r*)_{H-H} appears around 1.5 Å, showing H–H interactions between the same water molecules. The second peak in g(*r*)_{H-H} appears around 2.3 Å, showing the interaction between H atoms of different water molecules. The first peak in g(*r*)_{O*-H} is 1.0 Å and corresponds to the O–H bond. The second peak in g(*r*)_{O*-H}

appears at 1.6–2.1 Å, which shows strong hydrogen bonding between the H and O atoms in different water molecules. The first peak of $g(r)_{Zr^*-O^*}$ is 2.15 Å and corresponds to the interaction between the Zr atom on the surface and the O atom in a water molecule, which also indicates that the water molecules are strongly adsorbed and dissociated on the ZrO₂ surface. The value of the integral RDF corresponding to the first peak of $g(r)_{Zr^*-O^*}$ is 0.9, indicating that the first coordination layer of the Zr atom on the surface has 0.9 O atoms and the Zr atom has approximately one water molecule adsorbed on it. The peak of $g(r)_{O^{**}-H}$ between O atoms on the surface of ZrO₂ and H atoms in the water molecule is about 1.0 Å and further indicates hydroxyl (–OH) formation on the ZrO₂ surface. The value of the integrated RDF corresponding to the first peak of $g(r)_{O^{**}-H}$ indicates that the first coordination layer of the O atom has 0.4 H atoms on the surface. All these results above show that the water molecules mainly interact with each other via hydrogen bonding. The water molecules close to the surface will be strongly adsorbed at the Zr atoms on the surface to form Zr–O bonding sites. Meanwhile, the H atoms of some water molecules are dissociated to form O–H bonds with the O atoms on the surface.

The adsorption and dissociation behaviors of H₂O molecules on the ZrO₂ surface can be obtained by performing FPMD simulations of the water–solid interface of ZrO₂. Figures 7 and 8 show the evolutions of O–H and Zr–O bonds of the interface reaction between the first layer of water and the ZrO_2 surface, which is based on the four-membered ring (4MR) pathway. Initially, at the surface A site, the distance between the $O_{(1)}$ atom in the water molecule and the $Zr_{(1)}$ atom on the surface is around 6.1 Å. With the evolution of the FPMD simulation, the water molecules can go closer to the surface. At about 1000 fs, the distance between the $Zr_{(1)}$ and $O_{(1)}$ atoms decreases to around 2.141 Å, which implies the formation of Zr-O bonds. Similarly, the distance between the $O_{(1)}$ atom and the $H_{(1)}$ atom in the water molecule increases from 1.0 Å to 1.7 Å and the distance between the $H_{(1)}$ atom and the $O_{(2)}$ atom on the ZrO₂ substrate decreases from 5.0 Å to about 1.0 Å. All these indicate the breakage of the O-H bond in the water molecule and the formation of the H-O bond between the H atom in the water molecule and the O atom on the substrate surface. The distance between the $O_{(1)}$ atom and the $H_{(1)}$ atom remains around 1.7 Å, indicating that strong hydrogen bonds still exist between them. To verify the validity of the three-layer ZrO_2 model, we also performed FPMD simulations with a five-layer ZrO_2 surface model, shown in Figures 9 and S1. The simulation time of the FPMD was 1 ps. From Figures 9 and S1, we obtained similar behavior of the water-solid interface between three-layer and five-layer ZrO₂ surface models.



Figure 5. The three-layer model structure of the water–solid interface reactions of ZrO_2 .



Figure 6. Radial distribution functions (RDFs) and their integrated RDFs. $g(r)_{H-H}$ between H atoms in the water molecule (**a**), $g(r)_{O^*-H}$ between O atoms in the water molecule and H atoms in the water molecule (**b**), $g(r)_{Zr^*-O^*}$ between Zr atoms on the surface of ZrO₂ and O atoms in the water molecule (**c**) and $g(r)_{O^{**}-H}$ between O atoms on the surface of ZrO₂ and H atoms in the water molecule (**d**).



Figure 7. Evolutions of O–H and Zr–O bonds of the interface reaction between the first layer of water and the ZrO₂ surface at site **A**.



Figure 8. FPMD simulation snapshots at 0 (**a**), 1000 (**b**) and 3000 fs (**c**) of the water–solid interface reaction of ZrO₂ at site **A**.



Figure 9. Evolutions of O–H and Zr–O bonds in the interface reaction between the first layer of water and the ZrO₂ surface with the five-layer ZrO₂ model.

In addition to the dissociation of the first layer of water, the second layer of water on the surface also participates in the interface reaction. This water–solid interface reaction is based on the six-membered ring (**6MR**) pathway. Figures 10 and 11 show the evolutions of the bond lengths of O–H and Zr–O bonds at the reaction center. The whole reaction process involves the ZrO₂ surface at site **C** and two water molecules, $H_2O(a)(H_{(1)}O_{(1)}H)$ and $H_2O(b)(H_{(2)}O_{(2)}H)$, via a **6MR** pathway. In the beginning, the distances of the O₍₁₎ atom and H₍₁₎ atom, the H₍₂₎ atom and the O₍₂₎ atom are both 1.0 Å. The distances between the H₍₁₎ atom and O₍₂₎ atom, and H₍₂₎ and O₍₃₎ atom are 3.3 and 3.7 Å, respectively. The distance between Zr₍₁₎ and O₍₁₎ atoms is about 2.5 Å. At 500 fs, the H₍₁₎–O₍₂₎ and H₍₂₎–O₍₃₎ distances gradually become shorter and their distances both decrease to about 1.6 Å. The Zr₍₁₎–O₍₁₎ distance also decreases to 2.1 Å. All these indicate that H₍₁₎–O₍₂₎ and H₍₂₎–O₍₃₎ and Zr₍₁₎–O₍₁₎ bonds have the tendency to form. At 1400 fs, the H₍₁₎–O₍₂₎ and H₍₂₎–O₍₃₎

distances decrease to 1.0 Å. In contrast, the $O_{(1)}-H_{(1)}$ and $O_{(2)}-H_{(2)}$ distances increase to 1.7 Å. Afterward, the lengths of $O_{(1)}-H_{(1)}$ and $O_{(2)}-H_{(2)}$ bonds oscillate between 1.5 and 2.5 Å. At 2200 fs, the $O_{(1)}-H_{(1)}$ and $O_{(2)}-H_{(2)}$ distances oscillate around 3.0 Å. The distance between $O_{(2)}$ and $H_{(1)}$ is reduced to about 1.0 Å.



Figure 10. Evolutions of the bond lengths of O–H and Zr–O of two water molecules and the ZrO₂ interface reaction at site **C**.



Figure 11. FPMD simulation snapshots at 0 (**a**), 500 (**b**), 1400 (**c**) and 2200 fs (**d**) of the water–solid interface reaction of ZrO_2 at site **C**.

All these show that the H₂O (a) molecule can be dissociated to form the hydroxyl group, which can be strongly adsorbed to the $Zr_{(1)}$ atom on the substrate surface. This whole process of distance change shows that the dissociated H₍₂₎ atom in H₂O (b) dissociated from the H₂O (b) molecule can form a H₍₂₎–O₍₃₎ bond with the O₍₃₎ atom on the surface. The remaining hydroxyl portion of the H₂O (b) molecule can combine with the dissociated H₍₁₎

atom in H_2O (a) to form a new water molecule. DFT calculations and FPMD simulation results show that water molecules can not only be dissociated directly on the ZrO_2 surface but also exchange the proton with the help of adjacent water and finally be dissociated.

4. Conclusions

In summary, the adsorption and dissociation behaviors of water molecules on the surface of monoclinic ZrO₂ (111) were investigated using DFT static calculations and FPMD simulations. Four Lewis acid active sites of surface Zr atoms with different coordination environments have different adsorption and dissociation states and energies of water molecule on the ZrO_2 (111) surface. DOS analysis shows that the O atom of the water molecule prefers to bond with the Zr atom on the ZrO_2 (111) surface. There are strong interactions between the *p* orbitals of the O atom and the *d* orbitals of the Zr atom. The electrons of the *d* orbitals of the Zr atom on the surface fill the nonbonding orbitals of O atoms. H atoms of the water molecule prefer to bond with O atoms on the surface. Through FPMD simulations, the water-solid interface reaction of the ZrO₂ (111) surface was analyzed. The water molecules mainly interact with each other by hydrogen bonding. Through the 4MR or 6MR pathways of water-solid interface reactions, the first and second water molecules on the surface can be adsorbed and dissociated at the Zr sites on the surface to form Zr–O and O–H bonds. These insights can provide the theoretical significance for the adsorption and dissociation of water and the water-solid interface behavior of metal oxides, such as H₂O-based ALD.

Supplementary Materials: The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/nano12244362/s1, Figure S1: Radial distribution functions (RDFs) and their integrated RDFs of the interface reaction between the first layer water and ZrO2 surface on the five-layer ZrO2 model.; Table S1: Atomic coordinates of 2-layer ZrO2 substrate; Table S2: Atomic coordinates of 3-layer ZrO2 substrate; Table S3: Atomic coordinates of 4-layer ZrO2 substrate; Table S4: Atomic coordinates of 5-layer ZrO2 substrate; Table S5: Atomic coordinates of 3-layer ZrO2 substrate 55 waters.

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