The effect of oxygen vacancies on water wettability of a ZnO surface

Han Hu, a Hai-Feng Ji b and Ying Sun a

In this study, the effect of oxygen vacancies on the water wettability of a hydrated ZnO(100) surface has been examined via molecular dynamics simulations with a reactive force field (ReaxFF). The results show that the oxygen vacancies on the ZnO surface change the structures of the ZnO surface and subsequently its water adsorption capability. While a 1:1 ratio of water to hydroxyl is observed for a water monolayer adsorbed on ZnO(100) without oxygen vacancies, additional water adsorption as coordinate hydroxyl that resides on the vacancy site and bonds with three lattice zinc atoms is observed on the surfaces with oxygen vacancies. The results also show that the energy of the interaction per unit area between water and the hydrated ZnO surface is 55.1% higher in the presence of the oxygen vacancies than that without oxygen vacancies. This leads to a water contact angle of ~115° for the hydrated ZnO(100) surface in the absence of vacancies and ~21° with vacancies. The wetting kinetics of a water droplet on a ZnO(100) surface with and without oxygen vacancies are compared with the diffusion-limited reactive wetting and molecular kinetics models, respectively. In addition, the ordering of the vacancy sites is found not to significantly affect the wettability of the ZnO(100) surface.

1. Introduction

Surface wettability that is governed by surface chemistry and structure plays an important role in two-phase heat transfer,1 cell adhesion and protein adsorption,3 drug delivery,4 and microfluidics.5 Surfaces coated with stimuli-responsive organic compounds6–7 can achieve tunable wettability to enable the development of smart microfluidic devices (e.g., intelligent switches) but many of them have limited long-term durability. Surfaces with reversibly tunable wettability can also be realized by ultraviolet (UV) illumination of various transition-metal oxides, such as ZnO,8–12 TiO2,12–14 V2O5,15 and SnO2,16 and by ultraviolet (UV) illumination of various transition-metal oxides, such as ZnO,8–12 TiO2,12–14 V2O5,15 and SnO2,16 promise applications in self-cleaning,17,18 anti-fogging17,18 and microfluidics.5 Surfaces coated with stimuli-responsive organic compounds6,7 can achieve tunable wettability to enable the development of smart microfluidic devices (e.g., intelligent switches) but many of them have limited long-term durability. Surfaces with reversibly tunable wettability can also be realized by ultraviolet (UV) illumination of various transition-metal oxides, such as ZnO,8–12 TiO2,12–14 V2O5,15 and SnO2,16 and promise applications in self-cleaning,17,18 anti-fogging17,18 and microfluidics.5

Using ZnO as an example, the UV illumination generates electron–hole pairs on the ZnO surface, where some of the holes can react with lattice oxygen to form oxygen gas and surface oxygen vacancies.12 Preferential dissociative adsorption of water molecules at the oxygen vacancies results in a highly hydrophilic ZnO surface, where the water contact angle of a flat ZnO surface changes from 109° before UV illumination to 5° after UV illumination12 and the contact angle varies between >160° prior to UV illumination to ~0° after UV illumination for a rough or nanopatterned surface.13

By alternation of UV illumination and dark storage, the wettability variation is highly reversible and proceeds only at the outermost layer of the oxide film while the structure below remains stable to warrant long-term durability.

Several models have been proposed for possible adsorption structures of water on a transition-metal oxide surface after UV illumination. Evidence from X-ray photoelectron spectroscopy experiments has shown enhancements in both molecular and dissociative adsorption of water on ZnO,12 TiO2,12 and V2O5,15 surfaces. The enhanced water adsorption at vacancy sites due to UV illumination has been identified as a possible mechanism for photo-induced hydrophilic ZnO surfaces.9,11 Using thermal desorption spectroscopy (TDS), Sakai et al.13 identified two adsorbed hydroxyl structures on a TiO2 surface: hydroxyl bound to the oxygen vacancies that are coordinated to two lattice titanium atoms and dissociatively adsorbed water as adsorbed hydroxyl, which is coordinated to one lattice titanium atom. They hypothesized that the UV illumination converts one surface hydroxyl bound to the oxygen vacancy to two adsorbed hydroxyls, thereby increasing the total number of adsorbed hydroxyls on the TiO2 surface. However, the TDS experiments did not show an increased number of adsorbed hydroxyls after UV illumination. In addition, the adsorption structures of water on a ZnO surface after UV illumination are not well understood.

Molecular dynamic (MD) simulations are a powerful tool in obtaining an atomic level understanding of wetting phenomena19–22
especially on nanostructured surfaces,\textsuperscript{20} and are also used to investigate water adsorption on solid surfaces.\textsuperscript{21} Since photochemical reactions are involved in water adsorption on a transition-metal oxide surface with UV illumination, classic MD simulations are not capable of capturing the surface wettability change due to bond breaking and forming. A reactive force field technique, ReaxFF,\textsuperscript{24} has been developed to retain nearly all the accuracy of quantum mechanical (QM) calculations but allow MD simulations to run at costs comparable to simple force fields. ReaxFF uses the concept of bond order to model the interactions within a chemical system. By making each atomic interaction bond order dependent, a dynamic description of each atomic and molecular interaction is independent of the pre-defined reactive sites as opposed to those of empirical potentials. As a result, ReaxFF is able to capture the bond breaking and forming processes and has been successfully applied to metallic, covalent, and ionic bonds\textsuperscript{25–28} by allowing much larger systems than those using the QM methods. Recently, the ReaxFF method has been successfully extended to the ZnO–water system.\textsuperscript{29–31}

In this paper, the effect of oxygen vacancy on the wettability of water on a hydrated ZnO surface is examined via MD simulations with the ReaxFF force field to mimic the photochemical reaction processes of the water–ZnO system upon UV illumination. The ZnO(100) surface, the most energetically favorable surface of ZnO,\textsuperscript{32,33} is selected for the simulation because it is well understood and has been extensively investigated in experiments,\textsuperscript{34} quantum mechanical simulations\textsuperscript{32,35} and ReaxFF simulations.\textsuperscript{29} The simulation is first validated using the adsorption of a water monolayer on a ZnO(100) surface and then used to compute the interaction energy between a water film and a hydrated ZnO surface with and without oxygen vacancies. By analyzing the vibrational density of states of oxygen adsorbed on ZnO, new insights into adsorption structures of water on a hydrated ZnO(100) surface with oxygen vacancies have been proposed. Finally, the wetting kinetics and the contact angle of a water droplet wetting on a hydrated ZnO(100) surface with and without oxygen vacancies are examined and the results are compared with those from UV illumination experiments and model predictions.

2. Method

2.1 ReaxFF force field

In this paper, a reactive force field technique, ReaxFF,\textsuperscript{29} is incorporated into a large-scale MD simulator LAMMPS\textsuperscript{36} for MD simulation of water wetting on a ZnO(100) substrate with and without oxygen vacancies. Initially developed by van Duin et al.\textsuperscript{24} for H–C–O bonds, the ReaxFF method has been extended to oxides and the ZnO–water system.\textsuperscript{29–31} In ReaxFF, the general expression of interaction energy is given by

\[ E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{lip}} + E_{\text{val}} + E_{\text{vdW}} + E_{\text{Coulomb}} \]  

where \( E_{\text{bond}} \), \( E_{\text{over}} \), \( E_{\text{under}} \), \( E_{\text{lip}} \), and \( E_{\text{val}} \) stand for bond energy, over-coordination penalty energy, under-coordination energy, lone pair energy and valence angle energy, respectively; and are bond-order dependent. The van der Waals and Coulombic energy terms, \( E_{\text{vdW}} \) and \( E_{\text{Coulomb}} \), are non-bonded terms. Parameters of the ReaxFF potential for the ZnO–water system are constructed to fit with the QM results and experimental data in terms of surface energy, heat of formation, bulk moduli, and elastic constants of ZnO,\textsuperscript{20} as well as the adsorption energies and structures of water molecules on a ZnO surface.

2.2 Simulating oxygen vacancy

In order to mimic the effect of UV illumination on ZnO surfaces, oxygen vacancy sites are created on ZnO(100) surfaces in MD simulations. Fig. 1a shows the 3D view of a ZnO(100) surface with a vacancy site and Fig. 1b shows the zoomed-in top view of an oxygen vacancy site on a ZnO(100) surface. Once an oxygen vacancy (red square) is created at an arbitrary location of the ZnO topmost layer, the bond between the lattice zinc atom and the lattice oxygen atom (blue circle) next to this oxygen vacancy is enhanced. Thus, the energy barrier to create an oxygen vacancy in the neighborhood of the first vacancy becomes larger than other lattice oxygen sites. It is noted that the vacancy sites can be created on a ZnO surface as long as it follows the aforementioned criterion, either in a random or an ordered pattern. However, vacancies created in an ordered fashion allow for a larger number of sites in a given area than that of a random pattern. For example, as many as 667 ordered vacancy sites can be created on the ZnO(100) surface that has 2668 zinc and surface oxygen pairs within a cross-sectional area of 150.2 Å \( \times \) 148.2 Å, following the possible vacancy pattern shown in Fig. 1b. Randomly patterned vacancy sites that satisfy the aforementioned criterion however are less than 667. Fig. 1c and d show sub-sets of the ZnO(100) surface (the entire surface is too large to show) without vacancy and with 667 vacancy sites, respectively. Whereas, Fig. 1e and f show sub-sets of the ZnO(100) surface with 332 ordered and random vacancy sites, respectively.

2.3 Validation of MD simulations with ReaxFF

Adsorption of a water monolayer on a ZnO(100) surface without vacancies is first simulated to validate the MD simulations with the ReaxFF force field. Fig. 2b shows the simulation setup for the adsorption of a water monolayer on a ZnO(100) surface of 12.4 Å \( \times \) 75.1 Å \( \times \) 74.1 Å in dimension. Periodic boundary conditions are applied in all directions. The bottom layer of the ZnO substrate is held frozen at 0 K. A time step of 0.25 fs is used in all cases. After the water monolayer is placed on a ZnO(100) surface, a canonical (NVT) ensemble is performed at 10 K for the formation of bonds between water and the ZnO substrate. In all NVT simulations of the present study, the Nose–Hoover thermostat with a damping parameter of 100 fs is used to control the system temperature. The temperature of the system is then ramped up to 300 K for 25 ps and kept at 300 K for another 25 ps. The numbers of adsorbed water molecules and adsorbed hydroxyls are calculated to investigate the water adsorption structures on a ZnO(100) surface.

The formation energy of an oxygen vacancy on a ZnO(100) surface is then calculated to validate the MD simulations with
ReaxFF for simulating oxygen vacancy. A vacancy site is created on the top layer of a ZnO(100) substrate with a surface area of 9.83 Å × 10.55 Å. NVT simulations are performed at 300 K for both ZnO(100) surfaces with and without a vacancy site and the total energy is calculated over 25 ps. The formation energy of the oxygen vacancy is determined as the total energy difference between the ZnO substrate with and without the oxygen vacancy site. In subsequent simulations, the absorbed water monolayer is treated as a part of the substrate surface to form a hydrated ZnO surface, similar to the scenario when a ZnO substrate is exposed to moisture in the air.

2.4 Simulation cases

Four different sets of simulations with system setups shown in Fig. 2 are performed to investigate the effect of oxygen vacancies on wettability of ZnO surfaces. Firstly, the adsorption of a single water molecule is simulated to investigate the bond energy between O of H₂O and Zn of ZnO (Zn–H₂O bond). Secondly, the adsorption of a water monolayer on a ZnO(100) surface is simulated to study the chemical adsorption energy of the water monolayer, so as to infer the adsorption structure of the water monolayer. Thirdly, adsorption of a water film on a hydrated ZnO(100) surface is simulated to investigate water adsorption structures and the intermolecular interactions between the water film and the hydrated ZnO. Finally, the spreading of a water droplet on hydrated ZnO surfaces is simulated to study the wettability of the hydrated ZnO surfaces.

2.4.1 Adsorption of a single water molecule on a ZnO(100) surface. MD simulations with the ReaxFF force field are performed for adsorption of a single water molecule on ZnO(100) surfaces with and without vacancies to investigate the effect of oxygen vacancies on the Zn–H₂O bond energy. Fig. 2a shows a schematic of the setup with a surface area of 9.83 Å × 10.55 Å. A series of MD simulations with different Zn–H₂O bond lengths are performed to calculate the total potential energies. Each simulation is performed in an NVT ensemble at 300 K for 25 ps with the Zn–H₂O bond length kept constant.

The reaction profile is plotted as the total potential energy versus the length of the Zn–H₂O bond. The chemical adsorption energy, i.e. the energy released during the adsorption, is used to...
estimate the Zn–H₂O bonding energy and is calculated as the energy difference between the product and reactant, namely,

$$\Delta E = E_{\text{product}} - E_{\text{reactant}}$$ (2)

where $E$ represents the total potential energy and the subscripts reactant and product represent the simulation system before and after chemical adsorption, respectively.

### 2.4.2 Adsorption of a water monolayer on a ZnO(100) surface.

MD simulations with the ReaxFF force field are performed for adsorption of a water monolayer on ZnO(100) surfaces with and without vacancies to investigate the effect of oxygen vacancies on adsorption structure in the water monolayer. Fig. 2b shows a schematic of the setup with a surface area of 75.1 Å × 74.1 Å. For a ZnO surface without vacancies, the water monolayer adsorption is simulated with the same procedure stated in Section 2.3. For a ZnO surface with vacancies, the vacancy sites are created on an equilibrated hydrated ZnO surface based on the pattern shown in Fig. 1d. After oxygen vacancies are created, a subsequent NVT ensemble is performed at 300 K for 25 ps to equilibrate the hydrated ZnO(100) surface in the presence of oxygen vacancies.

The chemical adsorption energy is used to infer the number of bonds during adsorption and thus to study the water adsorption structure. The chemical adsorption energy of the water monolayer on ZnO surfaces with and without vacancies is calculated using eqn (2).

### 2.4.3 Adsorption of water film on hydrated ZnO(100) surfaces.

MD simulations with the ReaxFF force field are performed for the adsorption of a water film on hydrated ZnO(100) surfaces with and without vacancies to investigate the effect of oxygen vacancies on intermolecular interactions between water film and hydrated ZnO surfaces and water adsorption structures of the water film and the monolayer. Fig. 2c shows a schematic of the setup, including a 3 nm-thick water film on the equilibrated and hydrated ZnO(100) surface with and without oxygen vacancies. As shown in Fig. 2c, water molecules from the film represented by green and pink spheres (with green for hydrogen and pink for oxygen) are distinguished from those in the water monolayer using blue and red spheres (with blue for hydrogen and red for oxygen). An NVT ensemble is then performed for 25 ps to equilibrate the system consisting of water film and a hydrated ZnO surface.

To better understand the intermolecular interactions between water and ZnO, the interaction energy per unit area, $W$, between water and the hydrated ZnO(100) surface with and without oxygen vacancies is calculated using\(^{37}\)

$$W = \frac{E_{\text{water}} + E_{\text{surface}} - E_{\text{merged}}}{A}$$ (3)

where $E_{\text{water}}$ and $E_{\text{surface}}$ are the total energies of water and the hydrated ZnO(100) surface at 300 K, respectively, $E_{\text{merged}}$ is the total energy of a water film on a hydrated ZnO(100) surface equilibrated at 300 K, and $A$ is the nominal contact area of the water–hydrated ZnO interface. It is noted that the interaction energy per unit area is a different concept from the chemical adsorption energy defined by eqn (2). The chemical adsorption energy represents the energy released during adsorption due to formation of chemical bonds while the interaction energy per unit area is due to the van der Waals interactions and hydrogen bonds and represents the wettability of the hydrated ZnO surface.

The vibrational density of states (VDOS) can be used to represent vibrational properties of a material\(^{38}\) and are calculated to study the water adsorption structures of water film and the monolayer. Because oxygen atoms have different vibrational properties in different states (e.g., H₂O versus OH), the peaks in the VDOS of oxygen can reveal different water adsorption structures. In this study, VDOS of oxygen in a water film absorbed on a hydrated ZnO(100) surface are calculated using the Fourier transform of the velocity auto-correlation function (VACF) defined as

$$F(\omega) = \int_{-\infty}^{+\infty} Z(t) e^{-i\omega t} dt$$ (4)

where $t$ and $\omega$ are time and frequency, and $Z(t)$ is the VACF given by\(^{39}\)

$$Z(t) = \langle \psi(t) \psi(0) \rangle$$ (5)

Here, $\psi$ is the velocity vector of an atom and the symbol $\langle \rangle$ stands for time average. At zero frequency,\(^{40}\) the real part of the VDOS becomes

$$\text{Re}[F(0)] = 6D$$ (6)

where $D$ is the self-diffusion coefficient. In this study, the square modulus of Fourier transfer of the VACF is used to represent VDOS, namely, VDOS = $|F(\omega)|^2$.

### 2.4.4 Spreading of a water droplet on a hydrated ZnO(100) surface.

To examine how water adsorption structures affect the wettability of a ZnO surface, MD simulations have been performed for a water droplet wetting on a hydrated ZnO(100) surface with and without oxygen vacancies as shown in Fig. 2d. For the surface with vacancies, a ZnO surface with 667 vacancy sites simulated with the same procedure stated in Section 2.3. For a ZnO surface without vacancies, the water monolayer adsorption is performed for a water droplet wetting on a hydrated ZnO(100) surface.

The water contact angle on the hydrated ZnO surfaces represents the wettability of the surfaces and is calculated as a function of the spreading time. To determine the time dependent radius $R(t)$ of the spreading droplet and the contact angle $\theta(t)$, layers are defined in the simulation cell parallel to the ZnO surface with a thickness of $x$ equal to 2 Å. Within each layer at a given $t$, the density of droplet atoms is calculated as a function of distance from the layer's center of mass. Density data are integrated until 98% of droplet atoms in the layer are accounted for; the distance at which this occurs is $R(t)$ for the layer $l$. The criterion of less than 100% is used to avoid erroneous data generated by single water molecules breaking away from the droplet. By performing this analysis in different water layers above the ZnO surface, the spreading radius $R(l)$ for $l = 1$, and the contact angle $\theta(l)$ determined by a linear fit to $l$ versus $R(l)$ data between the first and sixth layers above the substrate surface are calculated. It should be noted that some water molecules are evaporated from the droplet and these escaped single molecules with no adjacent water molecules within 3.1 Å are not included in the spreading radius and contact angle calculations.
Droplet wetting simulations were also performed on hydrated ZnO surfaces with ordered and random vacancy sites (Fig. 1e and f, respectively) in order to investigate the effect of vacancy ordering on the wettability. The simulation setup for the vacancy ordering study is the same as that shown in Fig. 2d except that 332 oxygen vacancy sites are created for each case on a ZnO(100) surface of 150.2 Å × 148.2 Å.

3. Results and discussion

3.1 Validation of MD simulations with the ReaxFF force field

The MD simulations with ReaxFF are first validated for adsorption of a water monolayer on a ZnO(100) surface without oxygen vacancies. The experimental evidence, QM calculations, and ReaxFF simulations at 300 K all indicate a half dissociation and a half molecular adsorption of a water monolayer on a ZnO(100) surface. Fig. 3 shows the calculated ratio of adsorbed OH to H$_2$O as a function of time, where the y-intercept denotes the initial ratio of OH to H$_2$O in the water–ZnO(100) system at 10 K. With the increase of system temperature from 10 K to 300 K, the ratio of adsorbed OH to H$_2$O continues to increase and finally reaches the ratio of one after the system maintains at 300 K. This finding agrees well with both QM calculations and experimental results from the literature.

The MD simulations with ReaxFF are then validated for the formation energy of an oxygen vacancy on a ZnO(100) surface. The calculated formation energy of an oxygen vacancy using ReaxFF is 3.4 eV, compared to that of 3.13 eV based on first principle calculations. This 8.9% discrepancy indicates that the ReaxFF can fairly accurately capture the vacancy formation of the ZnO surface.

3.2 Reaction profile and Zn–H$_2$O bonding energy

The reaction profiles for the adsorption of a single water molecule on a ZnO surface with and without oxygen vacancies are shown in Fig. 4. In the reaction profile, the ground state represents the reactant (i.e. no adsorption) and the lowest energy state represents the final product of the reaction (i.e. molecular adsorption). The energy difference between the product and the reactant is the chemical adsorption energy. In single water molecule adsorption, the water molecule is only molecularly adsorbed on both ZnO(100) surfaces with and without vacancies. Therefore, the chemical adsorption energy is only due to the formation of the Zn–H$_2$O bond. The energy of the Zn–H$_2$O bond for a single water molecule on a ZnO(100) surface without vacancies is 13.4 kcal mol$^{-1}$, which is very close to that of 12.7 kcal mol$^{-1}$ on the surface with vacancies. This result indicates that the oxygen vacancy and the partially coordinated Zn ions on the ZnO surface with vacancies have little effects on the energy of the Zn–H$_2$O bond.

3.3 Chemical adsorption energy

For a water monolayer adsorbed on ZnO(100) surfaces with an area of 75.1 Å$^2$, the chemical adsorption energy on the ZnO surface with vacancies is 70.34 kcal mol$^{-1}$, which is 58.0% higher than that without vacancies, 44.51 kcal mol$^{-1}$. This result indicates that more bonds are formed during adsorption of a water monolayer on a ZnO(100) surface with vacancies than without vacancies. Thus, it is inferred that more OH or H$_2$O are adsorbed or a new water adsorption state that includes more Zn–O bonds is created on the ZnO surface with vacancies.

3.4 Interfacial energy and water adsorption structures

The computed interaction energy per unit area between water and a hydrated ZnO surface with oxygen vacancies is 16.18 J m$^{-2}$, which is 55.1% higher than that without oxygen vacancies, 10.43 J m$^{-2}$. The stronger interaction energy at the water–ZnO interface in the presence of oxygen vacancies leads to the enhancement of water wettability of a ZnO surface.

![Fig. 3](image3.png)  
**Fig. 3** Ratio of adsorbed hydroxyl to adsorbed water for water monolayer adsorption on a ZnO(100) surface without oxygen vacancies. The system temperature ramped from 10 K to 300 K in the first 25 ps and then maintained at 300 K for 25 ps.

![Fig. 4](image4.png)  
**Fig. 4** Reaction profile of a single water molecule adsorbed on a ZnO(100) surface with and without vacancies. The inset shows the schematic of the reactant and the product.
enhancing the bonding energy between the O from H₂O and oxygen vacancy affects the wettability of the surface not by and a water monolayer on a ZnO surface, it is clear that the adsorption of a single water molecule is confirmed from the wettability of the surface in the next section. Based on the adsorption of a single water molecule and a water monolayer on a ZnO surface with vacancies, three peaks can be observed for the VDOS of oxygen from the adsorbed water monolayer: the oxygen from adsorbed water molecules at 0.85 THz, adsorbed hydroxyls at 3.67 THz, and coordinate hydroxyls at 2.92 THz. The peak at 2.92 THz only appears for the adsorbed water monolayer on a ZnO surface with vacancies, indicating a new form of water absorption structure – coordinate hydroxyl, where the hydroxyls coordinate into the oxygen vacancies and bond with three lattice zinc atoms. We assign this peak to hydroxyl, but not H₂O because it is well known that once water molecules complex with metal ions, such as Zn²⁺, the water molecules become more acidic, i.e. they dissociate more readily to hydroxyl with Zn²⁺ and release H⁺, which increases hydrophilicity and wettability of the surface. This is confirmed from the wettability of the surface in the next section. Based on the adsorption of a single water molecule and a water monolayer on a ZnO surface, it is clear that the oxygen vacancy affects the wettability of the surface not by enhancing the bonding energy between the O from H₂O and Zn from the ZnO surface but by increasing the number of binding sites. The realization of the coordinate OH demonstrates that more bonds are indeed formed during water monolayer adsorption on a ZnO(100) surface with vacancies than without vacancies, and therefore confirms the conclusion obtained from the adsorption of water monolayer on a ZnO surface. The intensity of the oxygen peak in the water film at around 0.45 THz on a hydrated ZnO surface with oxygen vacancies is smaller than that without vacancies, both denoted by dashed lines in Fig. 5a, indicating a stronger confinement of water on the ZnO surface with vacancies where the degrees of freedom of water molecular vibration are reduced. In addition, the self-diffusivity (the value of VDOS at zero frequency) of the water monolayer is close to zero, implying that the adsorbed water monolayer has become a part of the ZnO solid surface.

3.5 Wetting of a water droplet on a ZnO(100) surface with and without vacancies

Fig. 5 shows the VDOS of oxygen atoms in the water film adsorbed on a hydrated ZnO(100) surface with and without vacancies. As it can be observed, while the VDOS of oxygen from the water film has only one peak at around 0.45 THz, the VDOS of oxygen from the adsorbed water monolayer has two peaks for the surface of ZnO(100) without vacancies, of which the peak at the low frequency (0.87 THz) represents the oxygen from adsorbed water molecules and the peak at the high frequency (3.70 THz) represents the oxygen from adsorbed hydroxyls. For the ZnO(100) surface with vacancies, three peaks can be observed for the VDOS of oxygen from the adsorbed water monolayer: the oxygen from adsorbed water molecules at 0.85 THz, adsorbed hydroxyls at 3.67 THz, and coordinate hydroxyls at 2.92 THz. The peak at 2.92 THz only appears for the adsorbed water monolayer on a ZnO surface with vacancies, indicating a new form of water absorption structure – coordinate hydroxyl, where the hydroxyls coordinate into the oxygen vacancies and bond with three lattice zinc atoms. We assign this peak to hydroxyl, but not H₂O because it is well known that once water molecules complex with metal ions, such as Zn²⁺, the water molecules become more acidic, i.e. they dissociate more readily to hydroxyl with Zn²⁺ and release H⁺, which increases hydrophilicity and wettability of the surface. This is confirmed from the wettability of the surface in the next section. Based on the adsorption of a single water molecule and a water monolayer on a ZnO surface, it is clear that the oxygen vacancy affects the wettability of the surface not by enhancing the bonding energy between the O from H₂O and Zn from the ZnO surface but by increasing the number of binding sites. The realization of the coordinate OH demonstrates that more bonds are indeed formed during water monolayer adsorption on a ZnO(100) surface with vacancies than without vacancies, and therefore confirms the conclusion obtained from the adsorption of water monolayer on a ZnO surface. The intensity of the oxygen peak in the water film at around 0.45 THz on a hydrated ZnO surface with oxygen vacancies is smaller than that without vacancies, both denoted by dashed lines in Fig. 5a, indicating a stronger confinement of water on the ZnO surface with vacancies where the degrees of freedom of water molecular vibration are reduced. In addition, the self-diffusivity (the value of VDOS at zero frequency) of the water monolayer is close to zero, implying that the adsorbed water monolayer has become a part of the ZnO solid surface.

Fig. 6 shows simulation snapshots for every 50 ps of a water droplet wetting on a hydrated ZnO(100) surface with and without oxygen vacancies. The droplet spreads much faster in the presence of vacancy, where the apparent contact angle is much smaller. The calculated contact angles of a water droplet on hydrated ZnO(100) with and without oxygen vacancies are shown in Fig. 7. For the entire simulation time, the contact angle on the surface with oxygen vacancies is always lower than that without vacancies. After 120 ps, the contact angle of the water droplet on a hydrated ZnO(100) surface without oxygen vacancies reaches a constant value of 115°, similar to the experimental values of 103° before UV illumination in Huang et al. and 109° before UV illumination in Sun et al. The slight difference in the contact angle between the simulation results and experimental measurements may be due to different crystal orientations and roughness of the ZnO surfaces. While the ZnO(100) plane is used in the present simulation, ZnO(002) surfaces are used in the experimental studies of Sun et al. and Huang et al. In the presence of oxygen vacancies, the calculated contact angle of the water droplet on a hydrated ZnO(100) surface keeps decreasing and finally reaches 21° ± 1.5°. This result lies in between the contact angle of 37° reported experimentally by Huang et al. on a ZnO film of 450 nm thick after 5 h of 8 mW cm⁻² UV illumination and the contact angle of 5° reported by Sun et al. on a 400 nm-thick ZnO film exposed to 2 mW cm⁻² UV illumination for 80 min. The discrepancy in experimental values of the contact angle might be contributed by different surface roughness values, crystalline orientation, and environmental conditions. In the present simulation, the droplet spreads on a perfectly smooth hydrated ZnO(100) surface in the absence of air. The large difference in the wettability of water on a hydrated ZnO surface with and without oxygen vacancies further confirms our earlier results of different water–ZnO interaction energies for these two surfaces.

For both non-reactive and reactive wetting of a liquid droplet on a solid surface, models have been advanced to connect wetting kinetics to relevant driving forces and dissipation mechanisms using the power-law form of droplet spreading radius, \( R \), versus time \( t \), i.e. \( R \sim t^x \), where \( x \) is determined by the specific dissipation mechanism. Fig. 8 shows the \( R(t) \) versus \( t \) of a water droplet wetting on a hydrated ZnO(100) surface with
and without oxygen vacancies. For the surface without vacancies, equilibrium is reached after 210 ps as both the contact angle and the droplet spreading radius become constant. For the surface with vacancy, the contact angle reaches a constant after 210 ps, but the spreading radius keeps increasing due to the hydrophilic nature of the surface. As a result, the contact line reaches the edge of the simulation domain after 270 ps for the surface with vacancies. For a water droplet spreading on a hydrated ZnO surface without vacancies, the power law fitting of $R^a$ is performed within the first 210 ps to include only the spreading process, while for a water droplet wetting on a hydrated ZnO surface with vacancies, fitting is performed for the entire 270 ps. The curve-fitted power $a$ for the surface with vacancy is 0.2522, compared to that of 0.1709 without vacancies. The result implies that, in the absence of oxygen vacancy ($a = 0.1709$), molecular adsorption and desorption of water to and from the ZnO(100) interface is very likely to be the dominant dissipation mechanism during wetting, which leads to $a = 1/7 = 0.1429$ in the molecular kinetic wetting regime. For the surface with oxygen vacancies ($a = 0.2522$), diffusion of water molecules to the surface oxygen vacancies controls wetting kinetics. This mechanism satisfies the diffusion-limited reactive wetting theory that gives the power-exponent $a = 1/4 = 0.25$. A thin layer of adsorbed and coordinate hydroxyls is formed on the ZnO surface, which improves the wetting kinetics of water compared to unreacted ZnO. Fig. 9 and 10 show the contact angle and spreading radius as a function of time for a droplet wetting on a hydrated ZnO(100) surface with and without vacancies. The average discrepancy in the
The contact angle between the two cases is \( \sim 10\% \) and that for the spreading radius is \( \sim 4\% \), demonstrating that the vacancy ordering does not significantly affect the wettability of a ZnO surface. Defining the oxygen vacancy density as the number of vacancy sites per unit surface area, ZnO surfaces with 667 and 332 vacancy sites correspond to vacancy densities of 4.98 mol m\(^{-2}\) and 2.40 mol m\(^{-2}\), respectively. Fig. 11 shows the equilibrium water contact angle on hydrated ZnO surfaces as a function of oxygen vacancy density.

4. Conclusion

In this paper, the effect of oxygen vacancies on the wettability of water on a hydrated ZnO(100) surface is examined via MD simulations with ReaxFF. The results show that the interaction energy per unit area between water and a hydrated ZnO surface with oxygen vacancies is 55.1% higher than that without vacancies. This leads to a water contact angle of \( \sim 115^\circ \) for the hydrated ZnO surface without vacancies, compared to that of \( \sim 21^\circ \) with vacancies, both of which match well with experimental observations. By analyzing the VDOS of oxygen adsorbed on ZnO, the adsorption structure of a water monolayer on a ZnO(100) surface with oxygen vacancies reveals enhanced dissociative adsorption energy and a new state of adsorption, the coordinate hydroxyl. The results also show that, in the absence of oxygen vacancies, the wetting kinetics of a water droplet on ZnO(100) matches well with the molecular kinetic theory, whereas the diffusion-limited reaction kinetics predicts the wetting kinetics of a water droplet on Zn(100) for the surface with oxygen vacancies. The ordering of the oxygen vacancy sites does not significantly affect the wettability of a ZnO(100) surface. Knowledge obtained here is important in a large class of energy conversion applications involving ZnO and water.

Acknowledgements

Support for this work was provided by the National Science Foundation (No. DMR-1104835). Computational resources were provided by the Extreme Science and Engineering Discovery Environment (XSEDE) [Grant #TG-CTS110056]. Y. Sun acknowledges financial support through the AFOSR Summer Faculty Fellowship Program and fruitful discussions with Dr Andrey Voevodin, Dr Chad Hunter, Dr Vikas Varshney, and Dr Ajit Roy in the Materials and Manufacturing Directorate of the Air Force Research Laboratory.

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