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Atomic Layer Deposition of Zinc Oxide: Diethyl Zinc Reactions and Surface Saturation from First Principles

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Abstract

Zinc oxide thin films grown via atomic layer deposition have been under intense research for the past few years. Here we present a comprehensive density functional theory study on the atomic layer deposition of zinc oxide. The adsorption of diethyl zinc and subsequent surface reactions are studied on an ideal (100) ZnO surface as well as on a stepped surface in order to compare an ideal and a nonideal surface structures. Our results show that diethyl zinc adsorbs and reacts rapidly on the surface to form monoethyl zinc. Our calculations also show that the initial ligand-exchange reactions are preferred on the planar surface over the step surface. Further reaction from monoethyl zinc to adsorbed zinc atoms has a high reaction barrier. We present two surface structures for the saturated zinc oxide surface at the end of the diethyl zinc pulse corresponding to a low and a high temperature approximations that are in good agreement with the experiments.

Introduction

Zinc oxide is a wide band-gap semiconductor with potential in applications due to its interesting properties. For example, high transparency and tunable electrical conductivity make zinc oxide thin films useful in numerous applications from thin film transistors to solar cells while piezoelectric properties can be used in micro-electromechanical systems and sensors.¹⁻³

Over the years zinc oxide thin films have been produced with various methods, from sputtering to chemical vapor deposition.^{2,4,5} In the recent years, interest to deposit zinc oxide thin films using atomic layer deposition (ALD) has increased, due to the decreasing dimensions of microelectronic applications. ALD is based on sequential, self-limiting gas-solid reactions. The precursors are introduced into the reactor chamber separately, thus avoiding any gas-phase reactions. Precursors then saturate the surface, providing a self-limiting adsorption process leading to precise thickness control and uniform, pin-hole free thin films. Between alternating precursor pulses the reactor chamber is purged with inert

gas.^{6,7}

Apart from inorganic metal oxide thin films, zinc oxide is also a common material used in the so-called organic–inorganic hybrid thin films that have amassed in the recent years. The zinc oxide hybrid films – called zincones – are deposited with a combination of atomic layer deposition and molecular layer deposition (MLD). The forming hybrid thin films consist of alternating layers or segments of inorganic and organic material. Hybrid thin films present interesting possibilities for tuning the properties of nano materials.⁸ While *ab initio* modelling has been used to simulate particular parts of MLD experiments in the past,^{9,10} the computational modelling of the growth process is demanding as it requires a large simulation cells, inclusion of weak interactions relevant in the case of organic molecules and a detailed description of the substrate surface before the organic reactant pulse. For this reason, we will include in our calculations a computational estimate of the surface composition at the end of the diethyl zinc pulse.

Inorganic zinc oxide thin films are usually deposited using diethyl zinc (DEZ) and water as precursors. The common temperature range for deposition is 100-200 °C. Zinc oxide deposits in a polycrystalline form with various lattice orientations present, but the orientations are sensitive to the deposition temperature. At low temperatures (below 100 °C) the lattice orientation of (002) is dominant. Above 100 °C the (002) orientation diminishes and the (100) lattice orientation becomes dominant within temperature range of 160-200 °C. Above 200 °C the preferred orientation switches back to (002).^{6,11,12} The ideal reaction mechanisms for the DEZ/H₂O-process are considered to be

The monoethyl zinc (MEZ) can also react further on the surface:

The dominant end-product from the adsorption of DEZ is considered to be MEZ, so the mechanism 1b is usually omitted. The interplanar distances of zinc oxide planes in the hexagonal zinc oxide unit cell are 2.60 Å and 2.82 Å for (002) and (100) planes, respectively. The growth-per-cycle (GPC) for the zinc oxide ALD-process ranges from 1.7 Å to 2.1 Å depending on the temperature, so the growth ranges from 60 % to 80 % from an ideal monolayer growth.¹³

The straight-forward surface saturation through mechanism 1a has been contradicted by experiment. If all the active surface sites (i.e. surface hydroxyl groups) were covered with monoethyl zinc groups after the DEZ saturation, the mass change during the water pulse would be negative as the ethyl-ligands were replaced with hydroxyl groups. However, in their *in-situ* quartz crystal microgravimetry (QCM) analysis of the ALD of zinc oxide thin films, Yousfi *et al.* conclude that no mass-change is observed during the water pulse as would be expected from the mechanisms 1a and 2a. The mass change during the DEZ pulse is approximately 120 ng / cm⁻² within the temperature range of 140-180 °C and that the mass of the deposited film remains constant during the water pulse.

A Fourier transform infrared spectroscopy study of the ALD of zinc oxide thin films by Ferguson *et al.*¹⁴ show the expected oscillation between hydroxyl and ethyl saturation of the surface with respect to reactant pulses. The saturation of the surface with ethyl groups during a DEZ pulse can be clearly seen from the absorbance spectra. However, the authors note that the DEZ/H₂O process deviates from an ideal ALD process because the adsorption of diethyl zinc is not self-limiting. The film deposition seems to continue after the surface is saturated with ethyl-groups. Since zinc oxide is a semiconductor, the deposition of ZnO onto ZrO₂ nanoparticles increases the electrical conductance of the particles and leads to a larger background infrared absorbance. The ongoing deposition of zinc oxide film can be measured as the increase of the background absorbance at 2000 cm⁻¹. This background absorbance increases during the DEZ exposure even after the absorbance of the ethyl-peak has saturated. The increase of the background absorbance is not observed during the water

pulse and the authors conclude that the water pulse is self-limiting. The authors speculate that the apparent increase of the substrate absorbance might be due to surface decomposition of diethyl zinc according to the following mechanisms:

The gas-phase pyrolysis of diethyl zinc has been studied experimentally by Dumont *et al.*^{15,16} The activation energy for the pyrolysis of diethyl zinc is 2.3 eV. Ferguson *et al.* comment that the pyrolysis of diethyl zinc could help to explain the no-mass change during the H₂O pulse found in the QCM measurement as there would be more zinc atoms present on the surface than would be expected from pure MEZ saturation.

Computational simulation of atomic layer deposition using quantum chemistry has been a rising field in the past few years.^{17,18} Only few computational studies of the atomic layer deposition of zinc oxide has been published in literature. The atomic layer deposition of zinc oxide via DEZ/H₂O-process has been studied on hydroxylated silicon by Ren¹⁹ and on hydroxylated zinc oxide by Afshar and Cadien.²⁰ Both simulations used the so-called cluster-model where the reactive site of surface is described using a small gas-phase cluster. Cluster-models are often employed in ALD publications. However, because the model neglects the surface environment it can lead to substantial error. Tanskanen *et al.*²¹ studied the reaction free energies for binding of tetrakis(dimethylamido)tin (TDMASn) and DEZ on various OH-terminated zinc oxide surfaces using a periodic slab-model. They compared thermodynamic stability of different surface species and concluded that the consumption of reactive hydroxyl sites by multi-ligand TDMASn leads to the reduced growth of zinc oxide after a TDMASn pulse. In their study, the authors did not study the kinetics of these processes or the saturation limit of the surface during the deposition.

In this work we have studied the atomic layer deposition of zinc oxide during the diethyl

zinc pulse, using density functional theory. The initial stages of the thin films growth were studied on an ideal (100) ZnO surface as well as on a stepped surface. The focus of this work is on the surface reaction mechanisms during the DEZ pulse as well as estimating the surface composition of the surface at the end of the pulse.

Computational methods

The reaction pathways were studied using density functional theory as implemented in GPAW.²² The Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional²³ was used with grid spacing of 0.2 Å. The TS09 van der Waals -correction on top of the PBE functional was used as proposed by Tkatchenko and Scheffler.²⁴ The k-points sampling of the reciprocal space was done using $2 \times 2 \times 2$ Monkhorst–Pack grid for bulk calculations and $2 \times 2 \times 1$ for the surface calculations. All geometry optimizations were carried out to gradients smaller than 0.05 eV/Å.

Relaxed surface scan were employed in order to explore several different mechanisms with relatively low computational cost. A reaction coordinate was chosen (usually the bond length between certain atoms) and the surface was probed along the reaction coordinate using constrained optimization. All the barriers presented in the results are calculated using the nudged elastic band method.²⁵

Some short (few pico seconds) Born–Oppenheimer molecular dynamics simulations were carried out in order to find a suitable minimum on the potential energy surface (PES). Dynamic simulations were carried out using a small polarized double-zeta basis set and a Berendsen thermostat.

Results

Zinc oxide exists in wide range of temperature and pressure in the wurtzite crystal structure which is composed of two interpenetrating hexagonal closed-packed sublattices. All atoms

have tetrahedral coordination. Experimental lattice vectors for the wurtzite structure are $\vec{a} = 3.2501 \text{ \AA}$ and $\vec{c} = 5.2071 \text{ \AA}$.²⁶ The zinc oxide cell parameters were optimised by scanning the lattice vectors $\vec{a}$ and $\vec{c}$ with a $2 \times 2 \times 2$ simulation box. The optimal values for the lattice vectors were found to be $\vec{a} = 3.3499 \text{ \AA}$ and $\vec{c} = 5.2650 \text{ \AA}$, slightly larger than previously reported experimental and theoretical values.^{2,26,27}

The surface was modelled using the common slab model with periodic boundary conditions imposed. A slab thickness of six stoichiometric oxide layers was used, similar to a recent publication by Tanskanen *et al.*²¹ Convergence for the slab thickness was checked with respect to the surface energy of the slab²⁸ as well with respect to the adsorption energy of water at monolayer coverage (see supporting information). The size of the surface in the simulation box used in the calculations was 2×2 the primitive cell (corresponding to 48 atoms) with a surface area of $70.55 \text{ \AA}^2$. This surface cell contains four surface zinc atoms. These four sites work as an active sites in water adsorption.

Hydroxylation of ZnO

The (100) lattice orientation is the preferred growth orientation of ZnO thin films in the deposition temperature range of 160-200 °C.^{6,29} The nonpolar nature of the surface make it suitable for computational study.

The adsorption of water onto the (100) ZnO surface has been studied extensively in the literature.³⁰⁻³² Meyer *et al.*³⁰ studied the adsorption of water onto the (100) ZnO surface with diffraction measurements as well as scanning tunnelling microscopy and concluded that water forms a (2×1) superstructure with long-range order. This (2×1) structure is formed with every other water molecule being intact while every other water molecule is dissociated (see figure 1). Helium thermal desorption spectroscopy (He-TDS) data shows that this structure exists well up to temperatures close to the boiling point of water. The authors measured the binding energy of a water molecule to be -1.02 eV. Theoretical calculations using density functional theory confirmed the (2×1) structure and provided an adsorption

energy of -1.13 eV per water molecule, in good quantitative agreement with the experiment. Calculations also show that an isolated water molecule adsorbs molecularly onto the surface but at increased surface coverage the water arranges to a half-dissociated "key-lock" configuration.

Yan and Al-Jassim³¹ as well as Calzolari and Catellani³² find support for the previous results in their respective theoretical studies and conclude that the hydrogen bonds between neighbouring water molecules make the molecules adopt a "key-lock"-type structural arrangement. Yan and Al-Jassim state, however, that they were not able to confirm the strong lateral interactions that would result in an island-like growth process reported by Meyer *et al.* They note that a half-dissociated (2×2) structure is only 0.07 eV higher in energy and expect that at elevated temperatures both the (2×1) and (2×2) structures are present. They also note that oxygen vacancies on the surface significantly affect the adsorption behaviour of water, promoting the dissociation of water especially at higher vacancy densities.

Table 1: Averaged adsorption energies for water as a function of surface coverage. The units are given in eV per molecule. At full monolayer coverage the 2×2 simulation cell contains four water molecules, one on each surface zinc atom. Molecular adsorption is preferred at low surface coverage, but fully hydroxylated surface prefers partially dissociated structure and adopts the (2×1) periodicity that has been experimentally confirmed. Adsorption energies for configurations where water adsorbs molecularly are marked with an asterisk. The experimental result is obtained using Helium thermal desorption spectroscopy (He-TDS).

Surface coverage / θ	$\frac{1}{4}$	$\frac{1}{2}$	1
This work	-0.96*	-1.11*	-1.26
Yan & Al-Jassim ³¹	-1.10*	-1.11*	-1.30
Calzolari & Catellani ³²	-0.95*	—	-1.16
Meyer <i>et al.</i> ³⁰	-0.94*	-0.97*	-1.13
Experimental ³⁰	—	—	-1.02

Our results are in good agreement with the previous results. We find that at low surface coverage ($\theta \leq 0.25$) the water prefers molecular adsorption over dissociated adsorption. This energy difference is small, however, only 0.15 eV. Our results also agree with Yan and Al-Jassim³¹ in that the dissociated water prefers the "bridging" site between two zinc atoms

Figure 1: The fully hydroxylated ZnO (100) surface, a side view and a top view. The water forms a 2×1 periodic structure where half of the water molecules are dissociated and half are in a molecular form.

over a "terminal" site on top of a surface zinc atom. The energy difference between these two configurations is 0.14 eV.

As the surface coverage increases, the water adopts the "key-lock"-configuration and prefers a partially dissociated adsorption over molecular adsorption. Difference between the molecular and partially dissociated configurations is small, 0.10 eV, in agreement with the previous results.³⁰⁻³²

This fully hydroxylated surface was adopted as a starting point for the adsorption of diethyl zinc and the subsequent surface reactions. When one compares the gas-phase entropy of the adsorbing molecule to the adsorption energy to the surface, they are of the same magnitude at the process conditions (at 450 K temperature and 100 Pa water partial pressure the entropy of a gas-phase water is approximately 1.21 eV). As adsorbed molecules still retain a large entropy on the surface,³³ we conclude that the surface of the zinc oxide should be fully hydroxylated within the process conditions. At high temperatures the surface hydroxyl coverage is expected to decrease and for this reason diethyl zinc adsorption onto a bare zinc oxide surface was also studied. The same hydroxyl concentration as on the fully hydroxylated planar surface was used in the calculations on the stepped surface discussed below.

DEZ pulse on ideal (100) surface

During the deposition of zinc oxide thin films with ALD the as-deposited films usually have a high degree of crystallinity. The (100) lattice orientation is present in the polycrystalline films in a wide temperature range and is the prominent growth direction at temperatures from 160 to 200 °C.^{6,34} During the ALD-process, both diethyl zinc and water are sequentially introduced to the reactor at low partial pressures. Between the reactant pulses the reactor chamber is purged with inert gas in order to remove by-products and remains of the previous reactant. Pulse pressures of DEZ and H₂O can range from few pascals up to a few hundred pascals.

Here we present our results for the adsorption of DEZ and the subsequent ligand-exchange reactions, i.e. mechanisms 1a and 1b, on the hydroxylated (100) zinc oxide surface. The effect of surface ethyl coverage as well as the possible decomposition of diethyl zinc on the surface to produce butane are also investigated.

First dissociation

The fully hydroxylated (100) ZnO surface has two different oxygen sites to which the diethyl zinc can adsorb: the oxygen of the molecular water and the oxygen of the dissociated water. The adsorption of DEZ is preferred to the molecular water on the surface as illustrated in figure 2. Adsorption energy for a diethyl zinc to the molecular water is -0.74 eV while onto the dissociated water the adsorption energy is only -0.53 eV. The tighter adsorption bond is also reflected in the bond length between oxygen and zinc, the bond length being shorter on the stronger adsorption bond (2.54 Å vs 2.76 Å). The tetrahedral geometry of the hydroxyl group oxygen suggests that the adsorption bond between the DEZ and the hydroxyl group is formed with the Lewis-acidic zinc accepting the lone-pair of the oxygen.

Figure 2: The adsorption configuration of the diethyl zinc. The DEZ prefers the molecular water over dissociated water as an adsorption site. Due to the ethyl-groups the DEZ is a rather bulky adsorbate and partially blocks other potential adsorption sites from the surface.

At low DEZ surface coverage the ethyl-ligand is removed from the DEZ via a straightforward ligand-exchange reaction, producing ethane. Due to low binding energy to the surface and partial pressure of ethane in the reactor, this process can be viewed as irreversible. The ligand-exchange reaction does not occur between the DEZ and the adsorbent water molecule. For this mechanism the reaction barrier is large, despite of the fact that the water oxygen is four-coordinated (two bonds to hydrogen, one to the surface zinc and a weak bond with DEZ). A low barrier mechanism for this ligand-exchange reaction was found with the neighbouring hydroxyl group. This mechanism has a barrier of only 0.47 eV. Reaction energy for the ligand-exchange mechanism is exothermic with -0.69 eV.

During the ligand-exchange the water molecule to which the DEZ is adsorbed to, transfers one of its protons to the neighbouring hydroxyl group that participates in the ligand-exchange reaction. Thus, the hydroxyl group is left protonated even after the ligand-exchange reaction. The proton-transfer can be seen by comparing the water molecules to which the DEZ is bonded to in figures 2 and 3.

The ligand-exchange reaction occurs through a proton-transfer from the surface hydroxyl group to the ethyl-ligand (see figure 3). In the transition state the O-H bond of the hydroxyl group stretches from $0.98 \text{ \AA}$ to $1.18 \text{ \AA}$ and Zn-O bond between the adsorbate and adsorbent

decreases from 2.56 Å to 2.01 Å. This is close to the bond length of the end product monoethyl zinc that has a Zn–O bond length of 1.82 Å. The distance between the proton and the receiving ethyl carbon in the transition state is 1.51 Å. The Zn–C bond stretches during the mechanism from initial 1.97 Å to 2.15 Å. The monoethyl zinc resulting from the ligand-exchange reaction is bonded to two hydroxyl groups as illustrated in figure 4.

Figure 3: The transition state for the initial ligand-exchange reaction on the planar (100) surface. The ligand-exchange reaction occurs with the neighbouring hydroxyl group, not with the water molecule to which the DEZ adsorbs.

The diethyl zinc is a rather bulky molecule due to its ethyl-ligands. For this reason, the effect of the surface coverage to the energetics of the reaction mechanisms were investigated. Including a second DEZ next to the adsorbed DEZ slightly decreased the adsorption energy. The averaged adsorption energy for the two diethyl zinc molecules is -0.59 eV per molecule. The weakened adsorption bond is evident from the longer Zn–O bond lengths, 2.69 and 2.76 Å. While the increased surface coverage slightly affected the adsorption energy, the surface coverage evidently lowers the reaction barrier for the initial ligand-exchange reaction down to 0.23 eV. This change in the activation energy has a large effect on the overall reaction rate. The reaction was exothermic with -0.90 eV.

Adsorption of another DEZ next to the monoethyl zinc was found to be exothermic with an adsorption energy of -0.65 eV. The adsorption is slightly affected by the monoethyl zinc.

The adsorbed DEZ can go through a similar ligand-exchange reaction as an isolated DEZ. As was the case with two diethyl zincs, the barrier is lower than in the case of an isolated DEZ molecule, 0.28 eV. Thus, it would seem that, at least at moderate surface ethyl-coverage, the steric hindrance between adsorbate molecules does not diminish the rate of the initial ligand-exchange reaction on the surface but rather seems to increase it.

Figure 4: The monoethyl zinc on the hydroxylated zinc oxide (100) surface. The MEZ adopts a bridging site between two hydroxyl groups. In the second ligand-exchange reaction the ethyl-group accepts the proton from the hydroxyl group below the monoethyl zinc.

Second dissociation

We now consider the mechanism for the removal of the second ligand. After the first ethyl group has been removed, the monoethyl zinc (MEZ) is coordinated to two oxygens with the ethyl group pointing upward from the surface as illustrated in figure 4. In order for the ethyl group to react with any of the surface hydroxyl groups, the ethyl group has to bend down toward to surface. This causes significant strain on the system and results in a high reaction barrier. Several possible mechanisms were investigated using relaxed surface scans and the reaction barriers for the removal of the second ligand were found to be considerably higher than for the first ligand.

For an isolated monoethyl zinc, the mechanism with the lowest activation energy was found to be a reaction with the hydrogen from the dissociated water molecule bonded to a

native oxygen below the MEZ. The Zn–C bond of the monoethyl zinc is in 38° angle with respect to the xy-plane of the surface. This angle decreases to 17° as the ethyl-group bends down toward to surface to the transition state. This leads to a large activation energy of 1.42 eV for the ligand-exchange reaction. In the transition state, the Zn–C bond length increases from the initial 1.96 Å to 2.10 Å and the O–H and C–H bonds are 1.39 Å and 1.35 Å, respectively. The second ligand-exchange reaction is endothermic with 0.35 eV, but due to the large free energy gain at the release of ethane from the surface, the mechanism can be regarded as irreversible.

The addition of another monoethyl zinc on the surface does not considerably change the reaction barrier for the ligand-exchange reaction. The barrier for a similar reaction was calculated to be 1.52 eV. The mechanism was endothermic with reaction energy of 1.31 eV. This is a considerable change in energy and close to the free energy that is gained from the release of ethane. However, it was found that the system can evolve to a more relaxed structure, only 0.20 eV above in energy of the initial structure. This relaxation of the surface structure occurs basically without a barrier as was observed during a short molecular dynamics simulation.

Just as was the case with the first ligand-exchange reaction, an increase in the surface ethyl-concentration has no hindering effects on the energetics of the ligand-exchange reaction. With four monoethyl zinc surface groups present, the activation energy is lowered to 1.31 eV.

Mechanisms not involving ligand-exchange between the surface and the precursor have been proposed. As mentioned above, Ferguson *et al.*¹⁴ observed an increase in the background absorbance of the zinc oxide film even after the surface was saturated with ethyl-groups and thus concluded the adsorption of diethyl zinc was not self-limiting. The authors proposed that decomposition of diethyl zinc may take place on the surface through mechanisms 1c and 1d.

We have investigated the formation of butane on the surface i.e. the mechanism 1c.

Based on our calculations the formation of butane on the surface does not occur as reaction between a surface monoethyl zinc and a diethyl zinc as proposed by the reaction equation 1c but solely through the diethyl zinc. While investigating a reaction in which ethyl-ligands from both the monoethyl zinc and diethyl zinc react to form butane, the system preferred a two-step mechanism in which the diethyl zinc donates one of its ethyl-ligands to the monoethyl zinc. This ligand-transfer reaction has a small barrier of 0.50 eV.

This mechanism is a simple ligand-transfer mechanism and does not lead to the formation of butane. From here the formation of butane occurred as the ethyl-ligands combined on the diethyl zinc. This reaction has a high barrier of 1.96 eV.

DEZ adsorption onto bare (100) surface

Since the surface of the (100) zinc oxide surface may not be fully hydroxylated, we investigated the adsorption of DEZ onto bare zinc oxide surface as an extreme case. We find that the DEZ adsorbs to the surface native oxide with adsorption energy of -0.94 eV which is 0.2 eV more exothermic than on the hydroxylated surface. This adsorbed configuration is only labile state and the DEZ can dissociate on the surface by donating one of the ethyl-ligands to a native zinc atom. The dissociation is barrierless and increases the adsorption energy to -1.34 eV. The ethyl-ligands are not removed from the bare surface by any acid-base process since there is no hydrogen present on the surface.

For two adsorbed DEZ the adsorption energy was calculated to be -0.96 eV per molecule, similar to a single adsorbed DEZ. Just as in the case of a single molecule, the adsorption energy for two dissociated DEZ molecules increased to -1.30 eV per molecule. At larger surface coverage the diethyl zinc start to experience repulsion between the ligands resulting in a smaller adsorption energy. For three adsorbed DEZ molecules the adsorption energy is -0.76 eV per molecule. For a dissociated configuration the adsorption energy increases to

Figure 5: Top view of the zinc oxide (100) surface and the orientations along which the two stepped surface were cleaved. The step **A** was produced by cleaving the (100) surface along (010) orientation one ZnO layer deep. Second step, step **B**, was cleaved along the (001) orientation.

−0.92 eV.

DEZ pulse on a stepped surface

The growth per cycle for a typical ALD process is usually less than a full monolayer due to the steric hindrance of adsorbed reactants.³⁵ The growth process may not lead to an ideal planar surface and in many processes the deposited film is amorphous. While the (100) lattice is a prominent growth direction during ALD within the temperature window of 160-200 °C, some of the film is deposited with random structure. Here we investigate the surface reactions on an amorphous structure constructed from the (100) surface by introducing a step onto the planar surface.

Two stepped surface were created from an ideal (100) surface by cleaving the top oxide layer of a seven oxide layers thick slab into half. The cleaving was done along the (010) (step **A**) and (001) (step **B**) orientations. The two cleaving directions are illustrated in figure 5. Four water molecules were then introduced on top of the the surface zinc atoms in order to produce the same surface coverage as for the ideal (100) surface.

Figure 6: The initial cleaved surface (above) and the resulting hydroxylated surface (below) on step **A**. The cleaved surface is the initial, unoptimised structure and the hydroxylated surface is the optimised structure after the *ab initio* molecular dynamic simulations. The left figures show the view along the (001) lattice orientation, while the figures on the right are from along the (010) orientation. When comparing the initial state to the optimised state, it is clear that during the optimisation the structure of the step switches to match that of the step **B**, seen in figure 7.

Molecular dynamic simulations were run for 2 ps at 550 K in order to remove strain from the system and to allow the system to evolve to a suitable relaxed configuration. Trajectories from these simulations were taken at 0.5 ps intervals and optimised. The lowest energy configurations were adopted for further calculations. The initial cleaved surfaces and the optimised hydroxylated structures for the surfaces **A** and **B** are presented in figures 6 and 7.

It is evident from the figures 6 and 7 that during the dynamic simulations the structure of step **A** came to resemble the structure of step **B**. The orientation of the steps on step **A** align to match the orientation on step **B**. This relaxation gives step **A** overall lower total

Figure 7: The initial cleaved surface (above) and the resulting hydroxylated surface (below) on step **B**. The cleaved surface is the initial, unoptimised structure and the hydroxylated surface is the optimised structure after the *ab initio* molecular dynamic simulations. The left figures show the view along the (001) lattice orientation, while the figures on the right are from along the (010) orientation.

energy than step **B**. On both surfaces a clear step remains after the optimisation. However, after the dynamic simulation the trench on step **A** is more crowded with water molecules and hydroxyl group, leading to overall more planar surface. On step **B** the trench remains wider and steeper .

Overall, due to the nonideal structure of the stepped surface and the amount of under coordinated surface atoms the adsorption energy of water was more exothermic than on the ideal planar surface and lead to dissociative adsorption. Estimations for the adsorption energy of water on the stepped surfaces were computed by removing the water molecules from the optimised hydroxylated configurations and comparing the change in energy. The adsorption energies were somewhat larger than on the planar surface, -1.64 eV and -1.81 eV for steps **A** and **B**, respectively. These hydroxylated, stepped surface were used to study the adsorption and ligand-exchange reactions of DEZ on an amorphous surface.

First dissociation

On step **A**, diethyl zinc adsorbed to a hydroxyl group on the terrace. The adsorption energy is smaller than on the planar (100) surface, -0.65 eV. The Zn–O bond length is 2.7 Å, slightly longer than on the planar surface. The adsorbed DEZ is illustrated in figure 8. From here the DEZ can undergo a ligand-exchange reaction by accepting a proton from the neighbouring hydroxyl group. Perhaps surprisingly, the barrier for this reaction is larger on the stepped surface than on the planar surface with the barrier being 0.90 eV. The transition state on the stepped surface is similar to the one on the planar surface. The ligand-exchange happens via proton transfer between the ethyl-group and the neighbouring hydroxyl group. The bond lengths in the transition state are close to the ones on the planar surface, but resemble a more late state in the proton transfer with a longer O–H bond and shorter C–H bond, 1.31 Å and 1.41 Å, respectively. The reaction is exothermic with a reaction energy of -0.42 eV.

Figure 8: The diethyl zinc adsorbed on the step **A**. On step **A** the adsorption is slightly less favourable and the barrier for the ligand-exchange reaction is considerably higher than on the ideal (100) surface.

On step **B** diethyl zinc preferred adsorption onto a hydroxyl group close to the trench. The adsorption energy for DEZ was larger than on the planar surface, -1.19 eV. The strong adsorption bond is reflected in the short Zn–O bond of only 2.0 Å. The adsorption structure

is shown in figure 9. While the DEZ is close to the hydroxyl groups on the step, it was found that the barrier for the ligand-exchange reaction is high, 0.93 eV, similar to step **A**.

Second dissociation

The end-products from the first ligand-exchange reaction on both surfaces are illustrated in figures 10 and 11. On both cases, the monoethyl zinc is situated near the step. On step **A** the monoethyl zinc undergoes a straight-forward reaction with the surface hydroxyl group. In the transition state of the reaction, the bond length between the accepting ethyl-group and the surface hydrogen is 1.42 Å, O–H bond is 1.27 Å and the Zn–C bond is 2.20 Å. The barrier for the mechanisms is of the same magnitude as on the planar surface, 1.59 eV, and the reaction is endothermic by 0.66 eV.

The ligand-exchange reaction on step **B** occurs in two steps: first the ethyl-ligand migrates from the adsorbed zinc atom to a native zinc atom. The end product is illustrated in figure 11. This migration of the ethyl group between the zinc atoms has a low activation energy of 0.19 eV and has a negligible reaction energy of 0.07 eV.

Figure 9: The diethyl zinc adsorbed on the step **B**. The adsorption is stronger on the step **B** than on planar (100) surface. The first ligand-exchange reaction has, however, a higher activation energy just like on step **A**.

Figure 10: The monoethyl zinc resulting from the first ligand-exchange reaction on step **A**. The activation energy for the second ligand-exchange reaction is similar to that on the planar (100) surface.

The ethyl-group can now react with a surface hydroxyl group. In the transition state the bond length between C–H, O–H and Zn–C are 1.34 Å, 1.38 Å and 2.20 Å, respectively. Judging from the bond lengths, the transition state on step **B** resembles the products more than on step **A**. The ligand-exchange reaction itself has a barrier of 0.95 eV, considerably lower than on the planar surface.

Surface saturation

The composition of surface in terms of DEZ, MEZ and Zn at the end of the DEZ pulse is an essential question in the deposition of zinc oxide. The saturated surface gives us several quantities that can be verified or falsified by experimental, such as the surface concentration in terms of ethyl-groups, the growth-per-cycle estimate or the mass-change during the DEZ and water pulses. This saturated surface can also be used as a starting point in investigating subsequent reactant pulses such as water or oxygen for inorganic thin films or organic molecules for inorganic–organic hybrid thin films.

With respect to various other precursors often used in ALD, the diethyl zinc is a simple molecule: the ethyl-ligands are relatively small compared to other precursors and react to inert by-products. Most importantly, DEZ has two ligands leading to only three possible

Figure 11: Monoethyl zinc on the step **B**. The monoethyl zinc resulting from the first ligand-exchange reaction between the diethyl zinc and a surface hydroxyl group is shown in the figures on the left. From this configuration, the ethyl-group migrates to a native zinc atom on the surface from which the ethyl-group can accept a proton as illustrated in the figures on the right.

stages of dissociation: diethyl zinc, monoethyl zinc and adsorbed zinc with no ligands. This makes the exploration of possible surface configurations feasible.

The surface composition depends on the kinetics of surface reactions as well as the thermodynamic stability of the resulting products. The kinetics for the first ligand-exchange reaction were shown to have a low barrier that was not hindered with increased surface coverage. However, the removal of the second ligand required considerably larger activation energy than the first ligand. Therefore two different approaches were taken in order to estimate the surface coverage at the end of the DEZ pulse: assuming that the diethyl zinc undergoes only the first ligand-exchange reaction as the second ligand-exchange reaction is blocked due to the high activation energy or that both the first and the second ligand-exchange reactions can occur in the process conditions. A more comprehensive estimation of the surface coverage at the end of the reactant pulse would require a kinetic simulation of the atomic layer deposition that is beyond the scope of this work.

In the first case the limiting factor of the process is the amount of monoethyl zinc that can form on the surface. It is assumed that steric effects between adsorbants do not considerably affect the kinetics of the first ligand-exchange reaction. In the second case we consider the possible configurations that can result considering that the second ligand-exchange reaction also occurs and that most or all hydrogens from the hydroxyl groups are consumed in the surface reactions.

Case 1: surface saturated with monoethyl zinc

Various configurations of monoethyl zinc terminated surface structures were created. Several 2-3 picoseconds long Born–Oppenheimer molecular dynamics simulations were carried out at 500 K and from the trajectories snapshots at 0.5 ps intervals were chosen and optimized. The formation energies for monoethyl zinc at different ethyl surface concentrations were calculated using the optimal configurations. The formation energies for monoethyl zinc terminated surfaces are given in table 2. The total energy change ΔE is the change in energy within the simulation cell with different monoethyl zinc surface coverage. The average formation energy, E_{ave} , is the total energy change averaged over the number of monoethyl zinc groups within the simulation cell:

$$\begin{aligned}\Delta E &= E(N) - E_{\text{surf}} - NE_{\text{DEZ}} + NE_{\text{C}_2\text{H}_6} \\ E_{\text{ave}} &= \frac{E(N) - E_{\text{surf}} - NE_{\text{DEZ}} + NE_{\text{C}_2\text{H}_6}}{N}\end{aligned}\tag{1}$$

where $E(N)$ is total energy of the cell containing N monoethyl zinc groups, E_{surf} is the total energy of the hydroxylated zinc oxide surface and E_{DEZ} and $E_{\text{C}_2\text{H}_6}$ are the total energies of a single diethyl zinc and ethane molecules in gas-phase, respectively.

The differences in the average formation energy between various structures are small. After the surface coverage of 5.7 MEZ nm⁻² there is a slight decrease in the average formation energy. This suggests that between the surface coverage of 5.7-7.1 MEZ nm⁻² the steric repulsion between the ethyl groups starts to make the formation of monoethyl zinc

Table 2: Monoethyl zinc formation energies at 0 K for monoethyl zinc as a function of surface coverage. The total energy change, ΔE , is the change in energy within in the simulation cell at different monoethyl zinc surface concentrations. The average formation energy, E_{ave} , is the total energy change averaged over the number of monoethyl zinc groups within the simulation cell. The configuration with six MEZ results in the formation of diethyl zinc and does not really correspond to a monoethyl zinc configuration.

MEZ coverage / nm^{-2}	1.41	2.83	4.25	5.67	7.09	8.50
Mass deposited, Δm / ng cm^{-2}	22	44	66	88	110	132
ΔE / eV	-1.43	-2.76	-4.55	-6.05	-7.21	-7.15
E_{ave} / eV	-1.43	-1.38	-1.52	-1.51	-1.44	-1.19

energetically less favourable. When the monoethyl zinc coverage increases to 8.5 MEZ nm^{-2} , two MEZ groups spontaneously form DEZ and Zn and no stable structure for this surface concentration was found. At this surface concentration the monoethyl zinc groups are no longer stable and the total formation energy is lower than at surface concentration 7.1 MEZ nm^{-2} .

Figure 12: Two side views from the saturated surface in case 1. The surface is saturated by monoethyl zinc with still some hydroxyl groups present.

The mass gain resulting from the various surface coverages is also included in the table

- The surface with the lowest formation energy has a surface ethyl-coverage of 7.1 Et nm^{-2}

and is illustrated in figure 12. This surface saturation corresponds to the mass gain of 110 ng/cm^{-2} which is in good agreement with the experimental values ranging from 100 to 120 ng/cm^{-2} ^{13,36,37} However, the expected mass-change during the water pulse would be -13 ng/cm^{-2} . This is based on the assumption that all the ethyl-ligands would be consumed in ligand-exchange reactions with water and that one water molecule would bond to one deposited zinc atom resulting in a stoichiometric film. This is in contradiction with the experimental data which strongly point out that no negative mass-change is observed during the water pulse.¹³

Case 2: surface covered with zinc and monoethyl zinc

If one assumes that the monoethyl zinc can undergo further ligand-exchange reactions, one can estimate the surface structure in the limit where most or all of the hydrogens from the surface hydroxyl groups are consumed. This leads to various possible surface structures.

The 2×2 simulation box contains in all eight hydrogen atoms (two from each water molecule). The extreme cases in which all the surface hydrogens are consumed can be calculated by recognizing that the formation of a single surface monoethyl zinc group consumes one proton from the surface and the formation of an adsorbed zinc atom consumes two protons. This leads to three possible combinations with different amounts of DEZ, MEZ and bare Zn. However, as shown above, the diethyl zinc dissociates on bare zinc oxide sites. This dissociation of diethyl zinc on the surface makes all the three possible configurations essentially the same configuration. The different configurations are discussed in more detail in the supporting information. The optimal configuration with the largest formation energy was selected as configuration I.

The configurations discussed above have lower surface MEZ concentration than the maximum concentration in case 1. Configuration with a higher MEZ concentration was constructed with five MEZ and one Zn atom (configuration II). In this configuration one of the eight surface hydrogens remains on the surface. A ligand-exchange reaction between the

surface hydroxyl group and a monoethyl zinc would lead to configuration I. The formation energies for the different surfaces are presented in table 3.

Just as in the case 1, the formation energies were calculated in the change of total energy per cell and also as an average over all the deposited zinc atoms:

$$\begin{aligned}\Delta E &= E(N + M) - E_{\text{surf}} - (N + M)E_{\text{DEZ}} + (N + 2M)E_{\text{C}_2\text{H}_6} \\ E_{\text{Zn}} &= \frac{E(N) - E_{\text{surf}} - (N + M)E_{\text{DEZ}} + (N + 2M)E_{\text{C}_2\text{H}_6}}{N + M}\end{aligned}\quad (2)$$

where E_{Zn} is the averaged formation energy per deposited zinc atom and $E(N + M)$ is the total energy of a surface containing N deposited monoethyl zinc groups and M deposited bare zinc. Rest of the terms are defined just as in equation (1).

Table 3: Formation energy at 0 K for different surface structures assuming that most of the hydrogen on the surface is consumed from during the adsorption of DEZ. The ΔE corresponds to the total energy change in the simulation cell obtained when compared to the hydroxylated (100) zinc oxide surface and ΔE_{Zn} is the energy change averaged over all the deposited zinc atoms as defined in equation (2) The Δm is the mass change during the deposition. The c_{ethyl} is the concentration of ethyl-groups on the surface. The units of energy are given in eV.

Configuration	DEZ	MEZ	Zn	ΔE	ΔE_{Zn}	$c_{\text{ethyl}} / \text{nm}^{-2}$	$\Delta m / \text{ng cm}^{-2}$
Configuration I	0	4	2	-8.19	-1.37	5.67	120
Configuration II	0	5	1	-7.35	-1.22	7.09	125

The lowest energy of the configurations considered was obtained for the configuration I, with formation energy of -8.19 eV or -1.37 eV per deposited zinc atom. The surface structure is illustrated in figure 13. This configuration corresponds to a mass-change of 120 ng/cm^{-2} , close to the experimental value observed. Assuming that during the subsequent water pulse all the ethyl-groups would react into ethane and one water molecule would adsorb to each surface zinc atom, the expected mass change during the water pulse would be very

Figure 13: Two side views from the saturated surface in case 2. The surface is saturated by monoethyl zinc with some deposited zinc atoms. No hydrogen is left on the surface.

small, only -2 ng/cm^{-2} . This value is well in line with the experimental observation that no mass-change is observed during the water pulse.

Discussion

DEZ adsorption on planar surface

The hydroxylation of the (100) zinc oxide surface as well as the adsorption of diethyl zinc and subsequent ligand-exchange reactions were studied. Our calculations on the adsorption of water onto the bare zinc oxide surface are in excellent agreement with previous studies and suggest that the zinc oxide surface is fully hydroxylated in the process conditions. The diethyl zinc is shown to adsorb exothermically to the hydroxylated zinc oxide surface with adsorption energy of -0.74 eV .

Our calculations show that the barrier for the **first ligand-exchange** reaction is small, at least at low to moderate surface ethyl concentrations. The barrier for the first ligand-exchange reaction ranges from 0.23 to 0.47 eV depending on the surface ethyl-coverage. The increase of neighbouring diethyl and monoethyl zinc had no inhibiting effect to the ligand-exchange reaction energetics, but the activation energy for the ligand-exchange reaction

seemed to lower considerably with increased surface concentration. This sort of cooperative effect of adsorbants has previously been reported for ALD in the growth of HfO_2 ³⁸ and Al_2O_3 .³⁹ However, this lowering of the reaction barrier is rather surprising as the neighbouring surface groups do not seem to directly affect the acidity of the surface hydroxyl groups by increasing the coordination number of the hydroxyl groups oxygen. Still, the decrease in the reaction barrier has a considerable effect on the overall reaction rates.

As the diethyl zinc adsorbs to the surface and undergoes fast initial ligand-exchange reaction, the surface rapidly becomes saturated with monoethyl zinc groups. A further dissociation from monoethyl zinc to adsorbed zinc through a **second ligand-exchange reaction** was also investigated. The barrier for this mechanism was estimated to be large, ranging from 1.31 to 1.52 eV. Thus, the second ligand-exchange reaction is considerably slower than the initial ligand-exchange reaction. At elevated temperatures this reaction may be feasible, assuming that all surface hydroxyl groups have not been consumed.

It has been shown by Ferguson *et al.* that the diethyl zinc pulse is not self-limiting but that an additional deposition of zinc occurs after surface saturation. This deposition has been suggested to occur between diethyl zinc and a surface monoethyl zinc via formation of butane or ethene and ethyne. A straight-forward mechanism was investigated for the production of butane and the reaction was found to have a large barrier of 1.96 eV. The reaction is not likely to be expected within the ALD of zinc oxide due to the high reaction barrier. From our calculations it would seem that zinc atoms are deposited during the ALD process but that no decomposition of diethyl zinc takes place. As the surface becomes rapidly saturated with monoethyl zinc the adsorption of diethyl zinc slows down and the monoethyl zinc slowly reacts with the remaining hydroxyl groups into bare zinc atoms. The slow second ligand-exchange reaction produces oxygen sites on the surface to which more diethyl zinc can adsorb to. As the second ligand-exchange is considerably slower than the adsorption rate of diethyl zinc, the surface ethyl-group concentration remains constant.

Only a few publications concerning the energetics of the atomic layer deposition of zinc

oxide exist in the literature. While it is known from experiments³⁷ that the ratio between deposited zinc atoms and the amount of consumed hydroxyl groups is larger than unity, the second ligand-exchange reaction is often omitted from any theoretical studies. A previous computational paper on the DEZ/H₂O-process by Afshar and Cadien²⁰ studied the homodeposition of zinc oxide. While the adsorption energy of the diethyl zinc reported by the authors is in good agreement with the results presented here, the cluster-model adopted by the authors considerably overestimates the barrier for the first ligand-exchange reaction, evaluating it at 1.34 eV. The second ligand-exchange is not studied in the paper.

A comparison with an experimental estimate can be extracted from the experimental kinetic model of Holmqvist *et al.* Their model on the DEZ/H₂O-process evaluated the barrier for the first ligand-exchange reaction to be 0.44 eV in an excellent agreement with our calculations.⁴⁰ However, the model did not include the second ligand-exchange reaction.

As an extreme case opposed to the fully hydroxylated zinc oxide surface, we studied the adsorption of diethyl zinc onto bare zinc oxide surface. The adsorption energy onto bare oxide surface was found to be larger than onto hydroxylated surface and zinc oxide was observed to dissociate barrierlessly by donating an ethyl-ligand to a native surface zinc atom. The dissociative adsorption onto an oxide surface means that at high temperatures when the surface is not fully hydroxylated, the diethyl zinc chemisorbs onto the surface. The adsorption energy for a single, dissociated diethyl zinc was -1.34 eV. The difference in the adsorption energy between the hydroxyl and oxide sites is relatively small when compared to e.g. trimethyl aluminium (TMA) on the (0001) aluminium oxide surface.^{41,42} The TMA reacts violently with the surface and dissociates by donating the methyl-ligands to the surface aluminium atoms resulting in a large adsorption energy of -2.56 eV. Interestingly, in the case of zinc oxide the difference in the surface reactivity between hydroxylated and bare oxide surface is not as large.

DEZ adsorption on stepped surface

In addition to an ideal (100) surface we also studied the adsorption of diethyl zinc on two stepped surfaces. Calculations on a stepped surface give a qualitative comparison between a crystalline and an amorphous zinc oxide surfaces. The stepped surfaces were more reactive toward water adsorption due to surface atoms with low coordination number as seen from the increased adsorption energy of water to the bare oxide surface. The effect of the step on the adsorption energy of diethyl zinc varied by being slightly smaller on step **A** (-0.65 eV) and considerably larger on step **B** (-1.19 eV).

A clear difference between planar and stepped surfaces was in the energetics of the **first ligand-exchange reaction**. The activation energy for the first ligand-exchange reaction was around 0.9 eV on both of the stepped surfaces. This barrier is considerably larger when compared to those calculated on the planar surface. The difference indicates that the formation of monoethyl zinc on an amorphous zinc oxide surface is a slow process and that the ligand-exchange reaction are preferred on a crystalline surface.

Energetics for the **second ligand-exchange reaction** differed on the two studied amorphous models. On step **A** the activation energy was similar to that of the planar surface with barrier of 1.59 eV. However, on the step **B** the barrier was considerably lower than on the planar surface. The step was found to play an important role in the second dissociation on step **B** since the ethyl-ligand of the monoethyl zinc was able to migrate to a surface native zinc from which it could react with a surface hydroxyl group more easily. Thus, the second dissociation was comprised of two processes. First the ethyl-migration to the native zinc atom that has a small barrier of 0.19 eV and the ligand-exchange reaction with a larger barrier of 0.95 eV. However, this barrier is still considerably smaller than any of the other mechanisms investigated for this ligand-exchange reaction and suggests that the second ligand-exchange reaction may occur through a more complex process than studied here.

Surface saturation

The surface composition at the end of the diethyl zinc pulse was estimated within two different assumptions. In the first assumption, the second ligand-exchange reaction was considered to be inaccessible at the process conditions due to the high activation energy of the reaction. This would give the configuration of the saturated surface at low deposition temperatures. The change in the total energy per simulation cell increased up to a surface concentration of 7.1 nm^{-2} . At larger surface monoethyl zinc concentrations the neighbouring monoethyl zinc groups reverted back to diethyl zinc. The adsorption of diethyl zinc and the kinetics of the first ligand-exchange reaction may be hindered at high surface coverage, so this concentration is an upper limit estimate for the surface concentration.

In the second assumption, we considered a surface where most or all of the surface hydroxyl group would have been consumed by both the first and the second ligand-exchange reactions. These configuration give the saturated surface at high deposition temperatures. Of all the tested configurations, the optimal configuration had a structure with an ethyl-concentration of 5.7 nm^{-2} , smaller than obtained in case 1. The configuration had effectively four monoethyl zinc groups and two zinc atom deposited on the surface. While the average formation energy for this configuration is smaller than in case 1, the free energy of formation is larger as more ethyl-ligands are released as ethane than in case 1 (eight vs. five).

These two estimated surface structures at saturation are in good agreement with experimental data and lay the foundation for a study of a subsequent reactant pulse. Our saturated surfaces corresponds to a QCM mass-change of 110 ng cm^{-2} (case 1) and 120 ng cm^{-2} (case 2), which is within the experimental range of about $100 \text{ to } 120 \text{ ng cm}^{-2}$.^{13,36,37} The low temperature estimate results with a negative mass-change during the subsequent water pulse. However, the formation of surface zinc atoms at elevated temperatures in case 2 leads to a negligible expected mass-change during the water pulse as observed in experiments. Also, the ratio between deposited zinc atoms and the amount of reacted hydroxyl groups on the surface in case 2, 1.33, is in excellent agreement with the experimental value measured by

Elam and George,³⁷ 1.37.

The amount of zinc oxide deposited in these two cases correspond to a growth-per-cycle of about 1.70 Å (case 1) and 2.05 Å (case 2), assuming that all the deposited zinc atoms react with water to form zinc oxide with density of 5.62 g cm⁻³. These GPC values are in good agreement with the experimental growth rates reported in the literature usually ranging from 1.7 to 2.1 Å.

Conclusion

The atomic layer deposition of zinc oxide on both a planar (100) and a stepped zinc oxide surfaces were studied from first principles. A fully hydroxylated zinc oxide surface was taken as the starting point for the deposition process and the kinetics of possible ligand-exchange reactions on the surface were calculated using density functional theory. The composition of the surface at the end of the diethyl zinc pulse was also studied.

Our calculations show that the formation of monoethyl zinc terminated surface is very rapid. The diethyl zinc adsorbs exothermically onto the hydroxylated surface and, contrary to previous computational publications, reacts with the surface hydroxyl groups with low barrier in good quantitative agreement with experimental estimates. The surface rapidly becomes saturated with monoethyl groups and at low temperatures stops to this point. At elevated temperatures the monoethyl zinc reacts to zinc atoms leading to increased deposition of zinc as more surface becomes available for diethyl zinc adsorption. The formation of zinc on the surface helps explain the no mass-change phenomena observed experimentally during the water pulse. We predict that no decomposition of diethyl zinc on the surface takes place during the deposition process. The difference of surface kinetics between an ideal (100) surface and a nonideal stepped surface was also investigated. It was found that the initial ligand-exchange reaction is preferred on a crystalline surface as the reaction barrier for the reaction is considerably larger on the amorphous surface when compared to a similar

mechanism on the planar surface. However, a lower barrier for second ligand-exchange reaction was found on the amorphous surface than on the crystalline surface, suggesting that surface defects such as steps may catalyse the second ligand-exchange reaction.

Two different models for the ethyl-saturated surface were studied, corresponding to a low temperature and a high temperature conditions. In our calculations the increase of surface coverage was not found to hinder the kinetics of the surface reactions and thus saturation is expected to be limited only by the steric repulsion of the ligands. The surface monoethyl zinc concentration at the saturation limit was estimated to be about $5.7 - 7.1 \text{ MEZ nm}^{-2}$. Our growth per cycle estimates for the two saturated surfaces range from $1.7 \text{ \AA}$ at low temperatures when no second ligand-exchange reaction occurs to $2.0 \text{ \AA}$ per cycle at higher temperatures, in excellent agreement with the experiments. These saturation estimates can be used to study the adsorption and kinetics of a subsequent reactant pulses.

Zinc oxide deposition via diethyl zinc and water is a common ALD process, of which only few theoretical studies have previously been published. The computational modelling of atomic layer deposition on the molecular level is very demanding as it requires large amounts of calculations to explore the possible configurations and reaction pathways on the surface. Our calculations on the ALD of zinc oxide are in good agreement with experiment and show that computational quantum chemistry is a feasible method for studying and predicting the thin film growth process. Computational simulations are necessary in understanding the complex mechanisms during the deposition process and are able to bring new information about the system.

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Supporting Information Available

Data on the convergence of the used surface slab model and additional information of the surface configurations studied in the case 2 of the saturated surfaces in Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

References

- (1) Zinc Oxide–Analogue of GaN with New Perspective Possibilities. *Cryst. Res. Technol.* **2004**, *39*, 980–992.
- (2) Morkoc, H.; Özgür, Ü. *Zinc Oxide: Fundamentals, Materials and Device Technology*; John Wiley & Sons, 2008.
- (3) Moezzi, A.; McDonagh, A. M.; Cortie, M. B. Zinc Oxide particles: Synthesis, Properties and Applications. *Chem. Eng. J.* **2012**, *185*, 1–22.
- (4) Kajikawa, Y. Texture Development of Non-Epitaxial Polycrystalline ZnO Films. *J. Cryst. Growth* **2006**, *289*, 387–394.
- (5) Park, W. I. Controlled Synthesis and Properties of ZnO Nanostructures Grown by Metalorganic Chemical Vapor Deposition: A Review. *Met. Mater. Int.* **2008**, *14*, 659–665.
- (6) Tynell, T.; Karppinen, M. Atomic Layer Deposition of ZnO: A Review. *Semicond. Sci. Technol.* **2014**, *29*, 043001.
- (7) Pinna, N.; Knez, M. *Atomic Layer Deposition of Nanostructured Materials*; Wiley-VCH, 2012.
- (8) Sundberg, P.; Karppinen, M. Organic and Inorganic–Organic Thin Film Structures by Molecular Layer Deposition: A Review. *Beilstein J. Nanotechnol.* **2014**, *5*, 1104–1136.

- (9) Karttunen, A. J.; Tynell, T.; Karppinen, M. Atomic-Level Structural and Electronic Properties of Hybrid Inorganic–Organic ZnO: Hydroquinone Superlattices Fabricated by ALD/MLD. *J. Phys. Chem. C* **2015**, *119*, 13105–13114.
- (10) Draxl, C.; Nabok, D.; Hannewald, K. Organic/Inorganic Hybrid Materials: Challenges for ab Initio Methodology. *Acc. Chem. Res.* **2014**, *47*, 3225–3232.
- (11) Yuan, N.; Wang, S.; Tan, C.; Wang, X.; Chen, G.; Ding, J. The Influence of Deposition Temperature on Growth Mode, Optical and Mechanical Properties of ZnO Films Prepared by the ALD Method. *J. Cryst. Growth* **2013**, *366*, 43–46.
- (12) Pung, S.-Y.; Choy, K.-L.; Hou, X.; Shan, C. Preferential Growth of ZnO Thin Films by the Atomic Layer Deposition Technique. *Nanotechnology* **2008**, *19*, 435609.
- (13) Yousfi, E. B.; Fouache, J.; Lincot, D. Study of Atomic Layer Epitaxy of Zinc Oxide by *in-situ* Quartz Crystal Microgravimetry. *Appl. Surf. Sci.* **2000**, *153*, 223–234.
- (14) Ferguson, J.; Weimer, A.; George, S. Surface Chemistry and Infrared Absorbance Changes During ZnO Atomic Layer Deposition on ZrO₂ and BaTiO₃ Particles. *J. Vac. Sci. Technol., A* **2005**, *23*, 118–125.
- (15) Dumont, H.; Marbeuf, A.; Bourée, J. E.; Gorochoy, O. Mass-spectrometric Study of Thermal Decomposition of Diethylzinc and Diethyltellurium. *J. Mater. Chem.* **1992**, *2*, 923–930.
- (16) Dumont, H.; Marbeuf, A.; Bourée, J.-E.; Gorochoy, O. Pyrolysis Pathways and Kinetics of Thermal Decomposition of Diethylzinc and Diethyltellurium Studied by Mass Spectrometry. *J. Mater. Chem.* **1993**, *3*, 1075–1079.
- (17) Elliott, S. D. Atomic-scale Simulation of ALD Chemistry. *Semicond. Sci. Technol.* **2012**, *27*, 074008.

- (18) Elliott, S. D.; Dey, G.; Maimaiti, Y.; Ablat, H.; Filatova, E. A.; Fomengia, G. N. Modeling Mechanism and Growth Reactions for New Nanofabrication Processes by Atomic Layer Deposition. *Adv. Mater.* **2015**, *28*, 5367–5380.
- (19) Ren, J. Initial Growth Mechanism of Atomic Layer Deposition of ZnO on the Hydroxylated Si (100)-2× 1: A Density Functional Theory Study. *Appl. Surf. Sci.* **2009**, *255*, 5742–5745.
- (20) Afshar, A.; Cadien, K. C. Growth Mechanism of Atomic Layer Deposition of Zinc Oxide: A Density Functional Theory Approach. *Appl. Phys. Lett.* **2013**, *103*, 251906.
- (21) Tanskanen, J. T.; Hagglund, C.; Bent, S. F. Correlating Growth Characteristics in Atomic Layer Deposition with Precursor Molecular Structure: The Case of Zinc Tin Oxide. *Chem. Mater.* **2014**, *26*, 2795–2802.
- (22) Enkovaara, J. e. Electronic Structure Calculations with GPAW: A Real-space Implementation of the Projector Augmented-Wave Method. *J. Phys.: Condens. Matter* **2010**, *22*, 253202.
- (23) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, p. 3865.
- (24) Tkatchenko, A.; Scheffler, M. Accurate Molecular van der Waals Interactions from Ground-state Electron Density and Free-atom Reference Data. *Phys. Rev. Lett.* **2009**, *102*, 073005.
- (25) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. *J. Chem. Phys.* **2000**, *113*, 9901–9904.
- (26) Kisi, E. H.; Elcombe, M. M. *u* Parameters for the Wurtzite Structure of ZnS and ZnO Using Powder Neutron Diffraction. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun* **1989**, *45*, 1867–1870.

- (27) Catlow, C. R. A.; French, S. A.; Sokol, A. A.; Al-Sunaidi, A. A.; Woodley, S. M. Zinc Oxide: A Case Study in Contemporary Computational Solid State Chemistry. *J. Comput. Chem.* **2008**, *29*, 2234–2249.
- (28) Fiorentini, V.; Methfessel, M. Extracting Convergent Surface Energies from Slab Calculations. *J. Phys. Condens. Matter* **1996**, *8*, 6525.
- (29) Wöll, C. The Chemistry and Physics of Zinc Oxide Surfaces. *Prog. Surf. Sci.* **2007**, *82*, 55–120.
- (30) Meyer, B.; Marx, D.; Dulub, O.; Diebold, U.; Kunat, M.; Langenberg, D.; Wöll, C. Partial Dissociation of Water Leads to Stable Superstructures on the Surface of Zinc Oxide. *Angew. Chem. Int. Ed.* **2004**, *43*, 6641–6645.
- (31) Yan, Y.; Al-Jassim, M. Structure and Energetics of Water Adsorbed on the ZnO (101̄0) Surface. *Phys. Rev. B: Condens. Matter* **2005**, *72*, 235406.
- (32) Calzolari, A.; Catellani, A. Water Adsorption on Nonpolar ZnO (1010) Surface: A Microscopic Understanding. *J. Phys. Chem. C* **2009**, *113*, 2896–2902.
- (33) Campbell, C. T.; Sellers, J. R. The Entropies of Adsorbed Molecules. *J. Am. Chem. Soc.* **2012**, *134*, 18109–18115.
- (34) Miikkulainen, V.; Leskelä, M.; Ritala, M.; Puurunen, R. L. Crystallinity of Inorganic Films Grown by Atomic Layer Deposition: Overview and General Trends. *J. Appl. Phys.* **2013**, *113*, 021301.
- (35) Puurunen, R. L. Surface Chemistry of Atomic Layer Deposition: A Case Study for the Trimethylaluminum/Water Process. *J. Appl. Phys.* **2005**, *97*, 121301.
- (36) Na, J.-S.; Scarel, G.; Parsons, G. N. *In situ* Analysis of Dopant Incorporation, Activation, and Film Growth During Thin Film ZnO and ZnO:Al Atomic Layer Deposition. *J. Phys. Chem. C* **2010**, *114*, 383–388.

- (37) Elam, J.; George, S. Growth of ZnO/Al₂O₃ Alloy Films Using Atomic Layer Deposition Techniques. *Chem. Mater.* **2003**, *15*, 1020–1028.
- (38) Shirazi, M.; Elliott, S. D. Atomistic Kinetic Monte Carlo Study of Atomic Layer Deposition Derived from Density Functional Theory. *J. Comp. Chem.* **2014**, *35*, 244–259.
- (39) Shirazi, M.; Elliott, S. D. Cooperation Between Adsorbates Accounts for the Activation of Atomic Layer Deposition Reactions. *Nanoscale* **2015**, *7*, 6311–6318.
- (40) Holmqvist, A.; Törndahl, T.; Magnusson, F.; Zimmermann, U.; Stenström, S. Dynamic Parameter Estimation of Atomic Layer Deposition Kinetics Applied to *in situ* Quartz Crystal Microbalance Diagnostics. *Chem. Eng. Sci.* **2014**, *111*, 15–33.
- (41) Elliott, S. D.; Greer, J. C. *J. Mater. Chem.* **2004**, *14*, pp. 3246–3250.
- (42) Weckman, T.; Laasonen, K. First Principles Study of the Atomic Layer Deposition of Alumina by TMA–H₂O-process. *Phys. Chem. Chem. Phys.* **2015**, *17*, 17322–17334.

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