

Force field for realistic molecular dynamics simulations of ZrO₂ growth



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ABSTRACT

The paper primarily deals with the development of an interaction potential (force field) for a realistic description of atom-by-atom ZrO₂ growth. Owing to the fact that for many metal oxides including ZrO₂ only full-charge (Zr⁺⁴ and O⁻²) interaction potentials are available, special attention is paid to the effect of the Zr and O elemental charges. Parameters of the short-range part of the interaction potential leading to experimental lattice parameters and formation energies have been identified in a wide range of elemental charges. Molecular dynamics simulations of ZrO₂ growth reveal that the structures grown using the presently available full-charge interaction potentials are in contradiction with an experiment (the atoms have too low coordination numbers). Simulations using a wide range of newly fitted full-charge and partial-charge interaction potentials reveal that the results depend (in addition to the fitting procedure) on the elemental charges. Correct partial charges and potential parameters leading to experimentally relevant structures (with correct coordination numbers) have been identified and used.

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1. Introduction

In recent decades, atomic-scale computer simulations became an invaluable tool supporting experimental research in the field of novel materials and novel techniques for materials preparation. There are two (currently) most important ways how to describe interatomic interactions in these simulations: (i) ab-initio simulations and (ii) classical simulations based on empirical interaction potentials (empirical force fields). The former technique is used for highly exact simulations dealing with a limited number of atoms (e.g. monocrystals or amorphous materials). The latter technique (which this work deals with) has orders of magnitude lower computational costs and therefore it is crucial for simulations dealing with much larger systems and/or longer time evolutions. More specifically, one of the most important and increasingly popular strengths of classical molecular dynamics (MD) simulations is that they allow one to reproduce the atom-by-atom growth of thin film materials (most often prepared by plasma-assisted physical or chemical vapor deposition) and to obtain a lot of related information not accessible experimentally [1–8]. The first reason is that contrary to experiments, MD simulations allow one to disentangle crystal nucleation and crystal growth (by using crystalline “substrate”). Second, they allow one to disentangle the effects of individual parts of the total particle flux (by modeling the impacts of individual particles). Third, they allow one to break the

correlation between process parameters (e.g. temperature and ion bombardment) by changing just one parameter at a time. Thus, these simulations were successfully used to describe the growth of C [5], Si [6], SiC [7], SiNH [8], SiO₂ [1], MgAlO [2], TiO₂ [3] or Al₂O₃ [4] (Ref. [4] also includes a more detailed overview).

The interaction potential choice is a critical factor for the success of classical MD simulations of the atom-by-atom film growth. Such a potential has to be (i) fitted using the same crystalline phase (s) which are supposed to grow and especially (ii) successfully tested by open surface growth simulations (the fact that the aforementioned crystalline phase(s) constitute local energy minima is in itself insufficient). In the case of ionic crystals the interaction potential obviously has to include not only a short range part but also a long range (Coulombic) part. The atomic charges may be either varied or fixed. The former choice [9–12] is crucial for special purposes, typically simultaneous description of qualitatively different environments of bonded atoms (e.g. Al/Al₂O₃ interface [10] or Zr corrosion [12]). However, within the large group of interaction potentials developed for other purposes than (and, consequently, during their development not tested by) open surface growth simulations, higher sophistication of the variable-charge potentials is not automatically correlated with better results of the growth simulations. For example, Ref. [4] shows that this choice may lead to even worse results. The latter choice, specifically the Buckingham interaction potential

$$U = Ae^{-r/\rho} - Cr^{-6} + q_1q_2/4\pi\epsilon r \quad (1)$$

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where r is the interatomic distance and $q_{1,2}$ are the charges), has been successfully used for atom-by-atom growth simulations [2–4,13,14] and may be therefore considered as a state of the art technique for modeling the growth of ionic metal oxides.

However, the list of available interaction potentials, even for many technologically important and relatively simple (binary) materials, is still limited. This constitutes an increasingly painful knowledge gap which prevents even stronger support of the experimental research in the aforementioned field by computer simulations. On the one hand, for some materials there are proper potentials which allow very successful simulations of the growth of the corresponding crystalline phases – see e.g. Ref. [3] (TiO₂) or 4 (Al₂O₃) for recent examples. On the other hand, for some equally important materials – e.g. ZrO₂, HfO₂ or Ta₂O₅ – either the potentials are completely unavailable, or (once again) there are potentials developed with a different simulation protocol in mind (e.g. annealing of existing crystals) and not tested (let alone developed) using open surface atom-by-atom growth simulations.

Fitting of a fixed-charge interaction potential includes (i) a choice of charges for all elements followed by (ii) a fitting of the short range part. Many researchers unfortunately use full charges (e.g. Zr⁺⁴ and O⁻²) without any discussion or clear physical basis. Such a choice is hardly supported by anything but simplifying the fitting procedure, and there are serious arguments against this choice. For example, Ref. [15] (dealing with Zr–Ca–O system) presents calculations predicting full charge (+2e) for Ca but partial charges for Zr (<+4e) and O (>-2e). In parallel, partial charge Buckingham potentials performed better than several full charge Buckingham potentials for both TiO₂ [3] and Al₂O₃ [4]. Moreover, full-charge potentials lead to higher (in some cases probably unrealistically high) potential energy of ionization (e.g. 91.65 eV per ZrO₂ formula unit for Zr⁺⁴ and O⁻², compared to 16.82 eV for Zr⁺² and O⁻¹) delivered into the growing films in addition to the kinetic energy.

Thus, the aims of this work are the following. First, to find out whether the currently available (full charge) ZrO₂ interaction potentials allow reliable MD simulations of ZrO₂ growth. Second (owing to the negative result of the first step), to develop partial-charge interaction potential(s) which describe the crystalline phases comparatively well as the full charge potentials. Third, to test these potential(s) by using them for simulations of ZrO₂ growth for various growth conditions and growth templates, and to identify the best one.

ZrO₂ was chosen for the presented investigations as an example of a technologically important and cost-effective material. ZrO₂ properties, ranging from mechanical strength and excellent thermal stability through high refractive index and ionic conductivity to high dielectric constant, lead to numerous applications such as diffusion and thermal barriers, ionic conductors, interference optical filters or high-k dielectrics in microelectronics [16–23]. Crystalline phases of ZrO₂ (ordered by increasing density and experimental interest) include monoclinic, tetragonal and cubic (m-, t- and c-ZrO₂, respectively). However, for the purpose of this paper ZrO₂ has to be understood predominantly as a test case. The qualitative phenomena shown below (e.g. the fitting procedure which allows one to effectively obtain partial-charge potentials) are expected to be valid for a wide range of other materials, especially ionic metal oxides, as well.

2. Methodology

This section (i) describes how the potential energy of ionization was included in the calculations, (ii) describes the calculations of crystal properties for a given interaction potential, (iii) describes the atom-by-atom growth simulations, and (iv) lists the presently

available full-charge ZrO₂ potentials considered. The fitting procedure of the partial-charge potentials is presented in the next section.

First of all, different elemental charges are associated with different potential energies of ionization (E_{ion}). The experimental formation energy is with respect to neutral atoms, while in fixed-charge simulations the formation energy is with respect to charged atoms. Thus, the potential energies of ionization (E_{ion}) have to be subtracted from the calculated energies before the latter can be compared with an experiment. Fig. 1 shows these energies for Zr and O in a range of charges (q_{Zr} and q_{O} , respectively) from zero to full. Quadratic dependencies were fitted to these energies: $4.6629q_{\text{Zr}}^2 + 0.3786q_{\text{Zr}} + 0.5117$ eV for Zr and $5.11q_{\text{O}}^2 + 6.58q_{\text{O}}$ eV for O. Assuming the charge neutrality ($q_{\text{Zr}} = -2 \times q_{\text{O}}$) this leads to

$$E_{\text{ion}} = 7.2179q_{\text{Zr}}^2 - 6.2014q_{\text{Zr}} + 0.5117 \text{ eV per ZrO}_2 \text{ formula unit.} \quad (2)$$

The same function was employed during the potential fitting (see Section 3.2).

All simulations were performed using the LAMMPS code [26]. Lattice constants and formation energies were obtained by calculating energies for at least five volumes (after a separate optimization of atomic positions in each case) and fitting the Birch equation of state:

$$E_V - E_0 = 9/8 BV_0([V_0/V]^{2/3} - 1)^2 + 9/16B(B' - 4)V_0([V_0/V]^{2/3} - 1)^3 \quad (3)$$

Here, V and V_0 is volume and preferred volume, respectively (corresponding to the energy E_V and the ground state energy E_0), respectively, B is bulk modulus at the volume V_0 and B' is pressure derivative of B . For the cubic phase (experimentally most interesting and primarily considered in this work) $V = a^3$ and for the tetragonal phase (considered in order to increase the transferability of the potentials fitted as much as possible) $V = a^2 \times c$ ($c/a = 1.016$ [27]). Various numbers of volumes (5, 7 or 9) and steps between individual volumes (2% or 4%), leading to only negligible differences, were used for cross-check purposes.

The film growth simulations were performed using periodic boundaries in horizontal directions, and a vacuum slab in the vertical direction. The recursive simulation protocol includes:

- (1) generation of the growth template (e.g. c-ZrO₂) and a 1 ps long “thermalization run” (canonical ensemble) at a given temperature, T (Nose–Hoover thermostat);

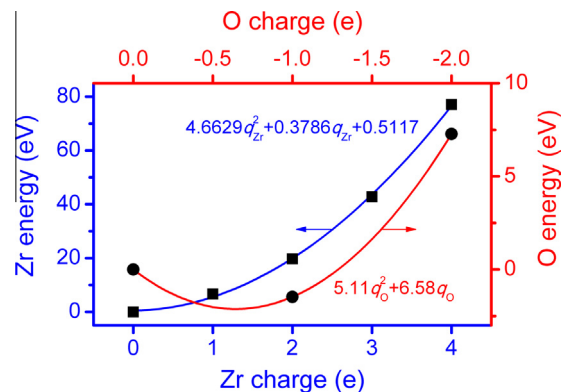


Fig. 1. Potential energy of ionization for Zr (squares; bottom and left axis) and O (balls; top and right axis) in a range from zero to full charges. The symbols (corresponding to integer charges) are sums of experimental ionization energies and electron affinities [24,25]. The lines are fits from a quadratic regression.

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