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A reactive force field (ReaxFF) for zinc oxide

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Abstract

We have developed a reactive force field (FF) within the ReaxFF framework, for use in molecular dynamics (MD) simulations to investigate structures and reaction dynamics for ZnO catalysts. The force field parameters were fitted to a training set of data points (energies, geometries, charges) derived from quantum-mechanical (QM) calculations. The data points were chosen to give adequate descriptions of (the equations of state for) a number of zinc metal and zinc oxide phases, a number of low-index ZnO surfaces and gas-phase zinc hydroxide clusters. Special emphasis was put on obtaining a good surface description. We have applied the force field to the calculation of atomic vibrational mean square amplitudes for bulk wurtzite–ZnO at 20 K, 300 K and 600 K and we find good agreement with experimental values from the literature. The force field was also applied in a study of the surface growth mechanism for the wurtzite(0001) surface. We find that the growth behavior depends on the presence of surface steps.

Keywords: Zinc oxide; Construction and use of effective interatomic interactions; Molecular dynamics; Density-functional calculations; Surface relaxation and reconstruction; Surface energy

1. Introduction

The aim of this study is to create a high-level, transferable interaction model for the condensed phases of zinc oxide. ZnO is a highly interesting material with a broad range of technical applications. It is known to catalyze a number of chemical reactions, such as the decomposition of formic acid and the formation of methanol from CO and H_2 [1–3]. Recent studies of ZnO nanostructures imply a connection between catalytic activity and surface morphology [1]. ZnO also attracts interest because of its electronic properties, with a semi-conducting band-gap of 3.4 eV. It has potential applications in opto-electronic devices, directly or as a substrate for the growth of other semiconductors such as GaN and SiC; here the interest in ZnO is partly fueled by the availability of high-quality substrates [4].

Because of this large versatility of ZnO, it is not surprising that a very large number of both experimental and theoretical studies of ZnO exist in the literature. Thus, for the various polymorphs of bulk ZnO only, numerous theoretical studies have been published, using models based either on quantum-mechanical (QM) methods (*ab initio* theory or density-functional theory (DFT)) or analytical force fields (FF). Some recent examples of such QM studies can be found in Refs. [5–7] (and references therein). In Ref. [5], Catti et al. studied the piezo-electric properties of ZnO using Hartree–Fock calculations, and in Refs. [6,7], the optimized geometry and electronic structure as well as the effect of pressure on the vibrations in several ZnO polymorphs were studied using DFT lattice dynamics.

The development of DFT techniques, or hybrid techniques such as the B3LYP functional [8,9], have resulted in methods that are significantly more efficient than *ab initio* methods of comparable accuracy. However, no

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DFT method available today is fast enough to describe chemical and physical properties accurately in large, dynamic systems with a few thousand atoms. Many systems with defects of various kinds and broken symmetries would ideally require such large systems. Therefore force field based methods are necessary.

ZnO is challenging to model by means of force field methods because of its partly covalent, partly ionic character. Traditionally, metal oxides have been modeled successfully using pair interactions consisting of a short-range part and long-range Coulombic terms, the latter usually modeled by fixing the charges of the different ions at their formal values. Such a procedure of course limits the possibility to describe a charge redistribution around a defect or at a surface. By adding an extra (charged) site to each ion connected via a spring, polarization can be handled; this is the idea behind the shell-model, [10] which can thus capture some of the many-body interactions, even in an otherwise pair-additive model. The short-range interactions in the shell-model are usually described by an analytical expression such as the Buckingham interaction model. Several successful attempts at using these schemes for ZnO can be found in Refs. [11–14]. In Ref. [11], a shell-model potential was used to predict the spatial arrangement of the dopant species sodium, lithium, and chlorine within the zinc oxide lattice in varistors using molecular dynamics (MD) simulations. The shell-model of Ref. [11] was also applied in the MD study of elastic properties of zinc oxide “nanobelts” in Ref. [14]. Whitmore et al. [12] used lattice dynamics calculations to parametrize a shell-model reproducing bulk vibrational properties of ZnO. This model has subsequently been applied to embed QM-clusters [13] in the investigation of electron trapping at the oxygen terminated polar (0001) surface of ZnO and related surface F centers.

The pure two-body potentials as well as the various shell models generally have difficulties in describing the covalent character of ZnO properly, as is evident from the fact that the four-coordinated wurtzite does not come out as the lowest-energy crystal structure in Refs. [11,12]. Instead, these models tend to favor the more isotropic, four-coordinated zincblende (sphalerite) structure. The description of covalent bonding can be aided by the use of explicit higher-order terms in the many-body expansion. One such example of the addition of a three-body interaction term can be found in the MD study of the growth mechanism for the ZnO(0001) surface in Ref. [15]. Another way to handle the covalent character of ZnO has been to neglect the ionic character altogether and use a *bond-order potential*, i.e. a potential where the short-range many-body effects depend on the local environment of each atom (the number of neighbors and the distances to them). This has recently been done in a successful way by Erhart et al. [16]. Such an approach might, however, have difficulties in modeling interfaces, or in other cases where Coulombic fields might be important. Moreover, if only nearest neighbors are considered, the model cannot describe the energy difference between the two four-coordinated ZnO phases. Incidentally, Ref. [16] gives an excellent review of different analytical potential schemes used for ZnO in the literature. In the present study, we will use the reactive force field (ReaxFF) framework to model ZnO.

The ReaxFF model [17–19] is also a bond-order interaction model. It is bond-order consistent for the two-body, three-body and four-body short-range interaction terms. The model also includes Coulombic terms, where the charges are calculated based on connectivity and geometry using the Electronegativity Equalization Method (EEM) [20], thereby allowing redistribution of charges. In principle these features allow the ReaxFF model to describe metallic, covalent and ionic bonds. The ReaxFF model is able to simulate the breaking and reforming phenomena of bonds during dynamics. It can also reproduce the structures and mechanical properties of condensed phases [17–19]. The ReaxFF framework was initially developed for hydrocarbons [17,18], and has since then been applied to many such systems. It has also been employed in the study of several oxide systems, namely MoO_x, V_xO_y and Bi_xO_y [21] oxides and Si/SiO_2 [18] and Al/Al_2O_3 [19] oxide interfaces.

All force field parameters within the ReaxFF framework are developed using results of quantum-chemical calculations. During the parametrization, measures are taken to provide for transferability, e.g. the parameters describing the oxygen–oxygen interaction are the same in all compounds and molecules. Therefore the set of data points to which the model is fitted needs to contain information about a wide range of compounds. In the current study this means having data not only for ZnO(s) and its surfaces, but also for Zn(s) and Zn and O containing gas-phase species. The ZnO parameters may thus in principle be used not only for the metal oxide but also for the metal/oxide interface and for systems where Zn or ZnO interact/react with hydrogen, hydrocarbons, and other interesting molecules (provided that a parametrization for the molecule is available and that the ZnO molecule cross-terms can be made).

However, parameterizing a model for a broad range of chemical environments might necessitate trade-offs. To ensure a good description of the most important parts of the data set, a weighting scheme is employed during the parametrization. In our case describing ZnO(s) and its surfaces were prioritized over the description of gas-phase hydroxide clusters. If future studies require greater accuracy for the gas-phase species, the weighting scheme could be redesigned to allow a closer reproduction of these data points.

The current parametrization of ZnO in the ReaxFF model consisted of the following steps: (i) The creation of an initial training set of data points (energies, charges and geometries) from QM calculations, (ii) selection of the appropriate number of terms in the ReaxFF energy expression, (iii) fitting the parameters to the training set, (iv) evaluating if the data set is satisfactorily reproduced or if the energy expression needs to be expanded with addi-