Computational Materials Science 142 (2018) 410–416

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

# Enhanced works of separation for (0 0 0 1)ZnO|(1 1 1)$ZrO_2$ interfaces via ion-doping in ZnO: Data-mining and density function theory study

Wenming Sun [a,*], Liang Zhang [b], Yanpeng Zhang [a], Jing Liu [a], Hong Wang [a], Yuxiang Bu [c]

[a] State Key Laboratory of Green Building Materials, China Building Materials Academy, 100041 Beijing, China
[b] NeoTrident Technology Ltd., 201204 Shanghai, China
[c] Department of Chemistry, Shandong University, 250100 Jinan, China

ARTICLE INFO

*Article history:*
Received 11 August 2017
Received in revised form 26 September 2017
Accepted 23 October 2017

*Keywords:*
ZnO
Interface
Work of separation
DFT

ABSTRACT

The enhanced works of separation for the low adhesive (0 0 0 1)ZnO|(1 1 1)$ZrO_2$ interfacess via Y-doping in ZnO slab were systematically studied using data-mining technique and density functional theory (DFT) study. The lattice constants in 31 types of doped wurtzite $Zn_{0.9375}X_{0.0625}O$ were evaluated from DFT calculations. No linear correlation is found between the lattice constants and atomic radii. A support vector regression (SVR) for the lattice constants of 32 $Zn_{0.9375}X_{0.0625}O$ has been performed. SVR method with leave-one-out cross-validation is used for evaluating the regression models. The correlation coefficient obtained by the models was 0.905. The accuracy of SVR model was higher than those of artificial neural network (ANN) and partial least square (PLS) methods. $Zn_{0.9375}Y_{0.0625}O$ has the largest lattice constants among the investigated systems. In Y-ZnO(0 0 0 1) surface, a significant segregation phenomena occurs. Hence, dopant Y expands the lateral lattice and leaves the Zn-terminal surface intact. For coherent (0 0 0 1)Y-ZnO|(1 1 1)$ZrO_2$ interfaces, Y-doping can enhance the work of separation significantly (~82%) compared with the undoped (0 0 0 1)ZnO|(1 1 1)$ZrO_2$ interfaces.



## 1. Introduction

The ZnO|$ZrO_2$ (or ZnO|Y-stabilized $ZrO_2$) oxide heterostructures have caused widely research interests because of their extensive industrial applications such as fabrication of high performance optoelectric devices [1–6] and resistive random access memory devices [7]. Till now, the studies on the adhesive strength of the interfaces are rare. In our previous work, we have determined that the works of separation for (0 0 0 1)ZnO|(1 1 1)$ZrO_2$ interfaces are low because of the large (~10%) lattice mismatch between ZnO and $ZrO_2$ surfaces [8]. A high interfacial adhesion is desirable in the long-term performance of oxide heterostructures. Naturally, decreasing the lattice mismatch between ZnO and $ZrO_2$ via ion-doping maybe a promising approach to enhance the adhesive strength. Because of their applications as diluted magnetic semiconductors and transparent conductive oxide thin films, electronic, magnetic and optic properties of doped ZnO have been extensively explored. Controllable doping or co-doping are easily achieved by substituting Zn with group-III elements (Al [9], Ga [10], Sc [11] and Y [12]), group-IV elements (Ge [13], Sn [14], Pb [15], Ti [16], Zr [17] and Hf [18]), group-I elements (Li [19,20], Na [21], Ag [22–25] and Cu [26,27]), and other elements such as V [28], Cr [26], Co [29], and Ni [30] or the combination of two cations.

These previous studies seem to offer us "abundant" samples to filter the suitable elements to decrease the lattice mismatch in ZnO|$ZrO_2$ interfaces. Typically, to create an X-doped ZnO (XZO) compound with X concentration of 6.25 at.%, a $2 \times 2 \times 2$ ZnO supercell model is constructed with substituting one Zn atom for X atom. However, in most of the theoretical studies, the lattice constants of doped ZnO were kept consistent with pure ZnO in order to save the computational time. The variations of lattice constants in $Zn_{0.9375}X_{0.0625}O$ were calculated only in few references. Among them, 9 types of elements (Sn [31], Ni [32,33], Cd [34,35], Cu [36], Ag [37,38], Ga [39], Al [40], Mg [41], and Fe [42]) were considered. Doping Cu, Ni and Fe has been determined to shrink the lattice constants insignificantly (less than ~0.3%). Doping Cd, Ga, Al and Al expands lattice constant no more than 1.0%. Yang determined that Sn-doping could expand the lattice constant by 3.0% [31]. Among these elements, only Sn enhances the lattice constant significantly. Due to the deficiency of data and the non-comparability of the available data originates from a wide variety of calculation methods, it is necessary to carry out a systematic investigation of the lattice constants in a series of XZO. Furthermore, constructing such a database is the first step to filter the

* Corresponding author.
*E-mail address:* swm@mail.sdu.edu.cn (W. Sun).

https://doi.org/10.1016/j.commatsci.2017.10.044
0927-0256/

suitable elements for enhancing the interfacial adhesion in ZnO|$ZrO_2$ heterostructures.

In the present work, we systematically calculated the lattice constants in 31 types of wurtzite $Zn_{0.9375}X_{0.0625}O$ by using DFT method. In order to reveal the relationship between the lattice constants of XZO and the atomic properties of X, several data-mining techniques were implemented. Yttrium was chosen and considered to enhance the adhesive strength ZnO|$ZrO_2$ heterostructures.

## 2. Methods and details

The calculations in this study were performed using the plane-wave pseudopotential method in the framework of DFT [43]. The ion core and valence electron interaction was described by Vanderbilt-type ultrasoft pseudopotential [44]. The exchange–correlation interactions were treated by the generalized-gradient approximation (PBE/GGA) scheme [45]. The kinetic energy cutoff was set to 400 eV. We chose a Monkhorst-Pack $4 \times 4 \times 2$ and $2 \times 2 \times 1$ k-point grids for the first Brillouin zone sampling in bulk and surface/interface calculations, respectively. The convergence thresholds between optimization cycles for energy change and maximum force were set as $10^{-5}$ eV/atom and 0.03 eV/Å, respectively. The (0 0 0 1)ZnO|(1 1 1)$ZrO_2$ interfaces were modeled by constructing a supercell containing 10 bilayers of ZnO (0 0 0 1) and 3 trilayers of $ZrO_2$ (1 1 1) plane using periodic boundary conditions.

A $2 \times 2 \times 2$ ZnO supercell model was considered, which contains 16 zinc and 16 oxygen atoms. Only one zinc atom was substituted with one other atom. The dopant concentration in bulk model is 6.25 at.%. The cell parameters of the XZO models (with 15 zinc atoms, 1 X atom and 16 oxygen atoms), in addition to their atomic coordinates were optimized fully.

Doped ZnO(0 0 0 1) surface and (0 0 0 1)XZO|(1 1 1)$ZrO_2$ interfaces are modeled by substituting one zinc atom in ZnO slab with X atom. For doped ZnO(0 0 0 1) surface model, the lateral lattice constants were also relaxed during the optimization. Based on our previous study, only Zn-terminated ZnO(0 0 0 1) surface was considered. Due to the polar character of ZnO(0 0 0 1) surfaces, the dangling bonds on the bottom layer are saturated with pseudo-hydrogens to prevent unphysical charge transfer between the bottom and top slabs. The interfaces between XZO(0 0 0 1) and $ZrO_2$(1 1 1) are modeled by constructing a supercell containing 10 bilayers of XZO(0 0 0 1) and 3 trilayers of $ZrO_2$(1 1 1) plane using periodic boundary conditions. All atomic coordinates of the coherent interfaces are allowed to fully relax. All the total energy calculations were performed using the CASTEP code [43].

## 3. Results and discussion

### 3.1. Data set available and descriptors selection

The calculated lattice constants for XZO as well as undoped ZnO are listed in Table 1. In the data mining procedure, a training set is implemented to build up a model, while a test set is to validate the model built. We can test the model by making prediction against the test set based on the value that determined for training set. Both training and test set can be selected by applying a random filter to the data. In the present work, the data were divided into 2 parts: undoped ZnO plus 24 XZO as the training set and 7 XZO as the test set. The candidate descriptors are listed in Table 2. These

**Table 1**
DFT calculated lattice constants for X-doped ZnO, where a, b and c are the lattice parameters (units: Å), α, β and γ are angles (units: degree). Table is divided into 2 part: 25 XZO as the training set and 7 XZO as the test set.

| X | a | b | c | α | β | γ |
|---|---|---|---|---|---|---|
| *Training set* | | | | | | |
| Zn | 6.564 | 6.564 | 10.592 | 90.00 | 90.00 | 120.00 |
| Ga | 6.575 | 6.575 | 10.634 | 90.00 | 90.00 | 119.98 |
| Al | 6.554 | 6.554 | 10.604 | 90.00 | 90.00 | 119.99 |
| Si | 6.577 | 6.577 | 10.612 | 90.00 | 90.00 | 119.97 |
| Na | 6.584 | 6.584 | 10.649 | 90.00 | 90.00 | 120.02 |
| Mn | 6.582 | 6.582 | 10.626 | 90.00 | 90.00 | 120.00 |
| Cd | 6.612 | 6.612 | 10.670 | 90.00 | 90.00 | 119.99 |
| Ti | 6.616 | 6.616 | 10.677 | 90.01 | 89.99 | 120.00 |
| Ge | 6.573 | 6.573 | 10.733 | 90.03 | 89.97 | 120.01 |
| Cu | 6.553 | 6.553 | 10.608 | 90.00 | 90.00 | 119.97 |
| Hf | 6.674 | 6.674 | 10.720 | 89.99 | 90.01 | 119.98 |
| Li | 6.539 | 6.539 | 10.564 | 90.00 | 90.00 | 120.00 |
| V | 6.589 | 6.589 | 10.625 | 90.01 | 89.99 | 120.00 |
| Ni | 6.567 | 6.567 | 10.576 | 90.00 | 90.00 | 120.00 |
| Fe | 6.569 | 6.568 | 10.605 | 90.00 | 89.99 | 119.99 |
| Cr | 6.596 | 6.596 | 10.582 | 89.99 | 90.01 | 120.03 |
| Y | 6.678 | 6.678 | 10.720 | 90.00 | 90.00 | 119.97 |
| Co | 6.565 | 6.565 | 10.599 | 90.00 | 90.00 | 120.01 |
| In | 6.624 | 6.624 | 10.697 | 90.00 | 90.00 | 120.00 |
| Sc | 6.612 | 6.612 | 10.639 | 90.00 | 90.00 | 119.99 |
| Zr | 6.658 | 6.658 | 10.710 | 89.96 | 90.04 | 120.01 |
| Pb | 6.628 | 6.628 | 10.779 | 89.99 | 90.01 | 120.00 |
| Sn | 6.606 | 6.606 | 10.780 | 90.00 | 90.00 | 120.01 |
| Ag | 6.590 | 6.639 | 10.676 | 90.01 | 90.01 | 119.96 |
| Er | 6.633 | 6.633 | 10.700 | 90.03 | 89.97 | 119.96 |
| As | 6.649 | 6.649 | 10.569 | 90.02 | 89.98 | 120.01 |
| *Test set* | | | | | | |
| Rh | 6.611 | 6.596 | 10.680 | 90.00 | 89.96 | 119.91 |
| Sb | 6.617 | 6.617 | 10.806 | 89.92 | 90.08 | 119.91 |
| Sr | 6.637 | 6.637 | 10.739 | 90.00 | 90.00 | 120.00 |
| Nb | *6.654* | 6.654 | 10.657 | 89.97 | 90.03 | 119.99 |
| Ru | 6.598 | 6.600 | 10.694 | 10.69 | 90.05 | 120.03 |
| Pd | 6.568 | 6.568 | 10.740 | 90.02 | 89.98 | 119.99 |
| Ba | 6.657 | 6.657 | 10.789 | 90.01 | 89.99 | 120.00 |