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First-principles study of diffusion of zinc vacancies and interstitials in ZnO

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ABSTRACT

A comprehensive investigation of zinc vacancy and interstitial diffusion in ZnO has been performed using *ab initio* total energy calculations with both the local density approximation (LDA) and the generalized gradient approximation (GGA). Zinc interstitial is found to diffuse efficiently with a small barrier, 0.3–0.5 eV. Therein, the diffusion perpendicular to *c* axis tends to occur via an interstitial mechanism, and the diffusion parallel to *c* axis tends to occur via a kick-out mechanism. The diffusion of the zinc vacancy is found to be isotropic, and the migration barrier of the zinc vacancy is about 1.0 eV. Based on our results, zinc vacancies are responsible for the self-diffusion of zinc for *n*-type ZnO.

1. Introduction

Zinc oxide (ZnO), with wide band gap (3.44 eV) and large exciton binding energy (60 meV), has obtained a large interest for potential applications in optical and optoelectronic devices [1]. The diffusion behaviors of intrinsic point defects in ZnO are fundamentally and technologically important. The annealing behavior of materials are determined by the diffusion of intrinsic point defects. The degradation of ZnO varistors is believed to occur via the migration of Zn interstitials to grain boundary regions [2]. The remarkable radiation hardness of zinc oxide is likely to be attributed to the annealing of defects by rapid defect migration [3]. Knowledge of diffusion of point defects is important for the understanding of their incorporation during growth and processing, and it is essential for modeling self-diffusion and impurity diffusion. Generally, dopant atoms move only when they are in one of their defective states as follows: dopant interstitial A_i, dopant vacancy pair AV or dopant interstitial pair AI. The diffusion behavior of vacancy and interstitial is essential for the understanding the diffusion of dopant atoms. A large number of experimental studies [4–19] and theory studies [20,21] have been conducted to study the self-diffusion of zinc in ZnO. However, the experimental results exhibit a considerable spread, which causes interpretation difficulty. Activation energies of zinc self-diffusion were reported to be in a range from 1.9 to 3.3 eV. Since the activation energy for self-diffusion is the sum of the formation energy of the defect that mediates the self-diffusion and its migration energy barrier [22], it is not straightforward to interpret these results, in which the formation energy of the defect strongly depends on the experimental conditions, such as the position of the Fermi level and the zinc or oxygen chemical potentials, which can cause large changes (by several eV). Therefore, a systematic theoretical investigation is highly desirable to separate the migration energy barrier from the activation energy and provide valuable insights into the various atomistic migration processes.

The purpose of this work is to comprehensively investigate the diffusion of zinc vacancies and interstitials in ZnO, by first-principles calculation and CI-NEB method. A novel non-symmetric configuration of zinc interstitial is found, presumably due to Jahn-Teller distortion. Zinc interstitials are found to diffuse efficiently both by interstitial mechanism and kick-out mechanism. The diffusion of zinc vacancy is found to be isotropic. Based on our calculation results, Zinc interstitials are fast diffusers, contributing to annealing processes, and zinc vacancies are responsible for the self-diffusion of zinc for *n*-type ZnO.

2. Calculational method and models

We perform our calculations both within the LDA [23] and GGA [24,25], since it is currently not understood which

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of these two flavors of density–functional theory give more accurate results. It is well-known that LDA overbinds molecules, solids and underestimate bonds and lattice distances, while GGA methods correct and sometimes overcorrect this. The difference between the results gives us an estimate of the error introduced by the exchange-correlation functional. The density functional calculations were carried out using the plane-wave based Vienna ab initio simulation package [26,27]. The electron wave functions were described using the projector augmented wave (PAW) method of Blöchl [28] in the implementation of Kresse and Joubert [29]. Plane waves have been included up to a cutoff energy of 400 eV. Electronic states were occupied with a Gaussian smearing width of 0.1 eV. A realspace projection scheme was used for efficient computations. Orthogonal suppercells containing 96 atoms were employed, with $a1 = 11.07$ Å, $a2 = 9.59$ Å, $a3 = 10.32$ Å for LDA and with $a1 = 11.38$ Å, $a2 = 9.85$ Å, $a3 = 10.59$ Å for GGA, which have lattice vectors $(0,2\sqrt{3}a,0)$, (3a,0,0), (0,0,2c). All calculations were carried out at the theoretical constant of bulk wurtzite ZnO. For integration within the Brillouin zone specific k points were selected using $2 \times 2 \times 2$ Monkhorst–Pack grids. The optimization procedure was truncated when the residual forces for the relaxed atoms were less than 0.01 eV/Å. The zinc 3d electrons were explicitly included in our calculations.

In order to obtain the energy barriers for the various diffusion paths we employed the climbing image nudged elastic band method [30,31] as implemented in VASP by Henkelman, Jonsson, and others [32], which is expected to be more reliable than dragging an atom from minimum to minimum across the estimated or guessed saddle point, especially in multiatom migration events. The images of CI-NEBM were relaxed until the maximum residual force was less than 0.01 eV/Å. Possible stable charges state of V_{zn} are 0, −1 and −2 and possible stable charge state of Zn_i is +2. All of them are included. For the charged state, a neutralizing background charge was imposed automatically in VASP calculations. The dynamic charged effect and band-gap correction are excluded from our consideration.

3. Results and discussion

3.1. Atomic geometry

First, we examined the structure of Zn interstitial. There are two distinct types of interstitial sites in the wurtzite structure: the tetrahedral site (tet) and the octahedral site (oct). The tetrahedral Zn interstitial was found to be unstable. The octahedral site is in the interstitial channel along the c axis. It is at the center of the hexagonal channel, as shown in Fig. 1(A). However, a novel metastable configuration was also found, as shown in Fig. 1(B), with only 0.03 eV (0.01 eV) higher energy than the symmetric configuration for LDA (GGA). We can see that, for this configuration, the Zn interstitial is not in the symmetric site, and one neighbor Zn atom is pushed noticeably down along c axis.

Second, we examined the structure of Zn vacancy. The oxygen atoms around the zinc vacancy exhibit outward relaxations. The O–O bond lengthes around the zinc vacancy extend average about 7%–11% with respect to the bulk O–O bond length for −2 charge state. The 0, −1 charge states are similar.

3.2. Diffusion mechanisms of Zn interstitial

For interstitial mechanisms, Zn interstitial migrates directly from one lattice interstice to another adjacent lattice interstice. We have considered two migration paths for Zn_i^{2+}, parallel and perpendicular to the c axis, respectively. We found that the Zn interstitial atom doesn't move through the unstable tetrahedral site in diffusion perpendicular to the c axis. The migration barrier

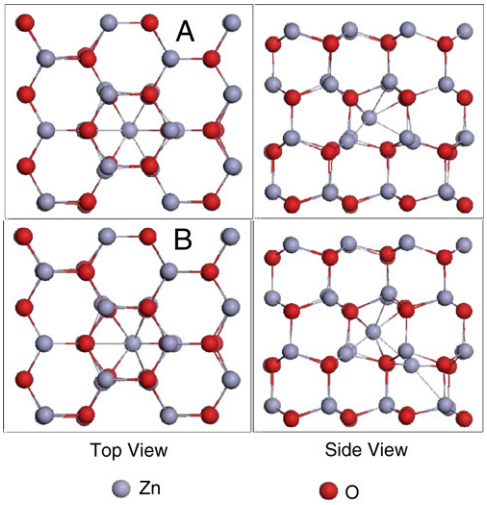

Fig. 1. Atom geometry of Zn octahedral interstitial.

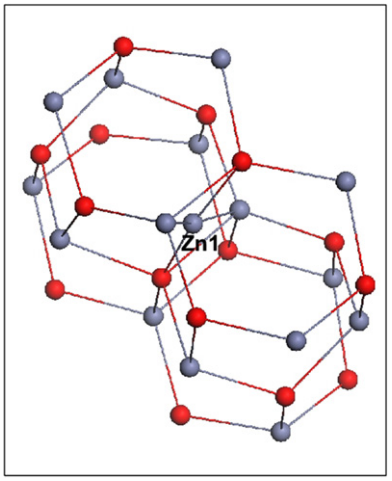

Fig. 2. The local atomic geometry of the saddle point of Zn_i^{2+} diffusion perpendicular to c axis.

for this path is 0.51 eV (0.03 + 0.48) for LDA, 0.34 eV (0.01 + 0.33) for GGA. Zn interstitial first moves from the symmetric site to non-symmetric site with 0.1 eV energy barrier, then moves through almost the center of the Zn–O quadrangle. The saddle point local atomic configuration is shown in Fig. 2. We can see that Zn_i is not at the tetrahedral site, different from the results of Janotti and Van de Walle [21]. Calculated energy along the migration path is shown in Fig. 3. We found that the diffusion path in which Zn_i^{2+} directly diffuses along the hexagonal channel is unstable for LDA, and would relax to the two steps kick-out mechanisms as follows. First, Zn kicks one of the nearest Zn substitutional perpendicular to c axis to octahedral interstitial site, and then the latter Zn atom kicks back into the lattice site, and pushes the original Zn atom parallel to c axis to octahedral interstitial. However, for GGA, this migration pathway is stable, the energy barrier is rather small, 0.54 eV, as shown in Fig. 4.

For kick-out mechanisms, Zn interstitial moves towards a substitutional Zn and then replaces it. We have considered two migration pathways for Zn_i^{2+} to kick the substitutional Zn out, parallel and perpendicular to the c axis. The Zn_i^{2+} first transforms to the non-symmetric configuration with energy barrier of 0.1 eV, and then undergoes the kick-out mechanism. Calculated energy along the migration pathway are summarized in Figs. 5 and 6. The energy barrier of kick-out mechanisms parallel to c axis is 0.45 eV for LDA, 0.36 eV for GGA. The energy barrier of kick-out