First-principles study of diffusion behaviour of point defects in the O-terminated (0001) surface in wurtzite ZnO*

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A detailed first-principles study of the diffusion behaviour of point defects in the O-terminated (0001) surface in wurtzite ZnO was performed. The O vacancy and interstitial are found to diffuse much more easily in surface than in bulk. The Zn vacancy has a similar migration barrier for both bulk and surface, but has much smaller barrier for the diffuse-in process. The Zn interstitial is difficult to diffuse in the surface directly, but it can diffuse into the bulk relatively easily. Specific values of corresponding migration barriers are obtained.

Keywords: semiconductor, surface diffusion, first-principles calculation
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1. Introduction

Zinc oxide (ZnO), with a wide band gap (3.44 eV) and large exciton binding energy (60 meV), has attracted large-scale scientific interest because of its potential applications in optical and optoelectronic devices.[1] The diffusion behaviour of intrinsic point defects in bulk ZnO is fundamentally and technologically important, and has been investigated extensively.[2−28] However, information on diffusion behaviour of intrinsic point defects in surface is limited. It is well known that intrinsic point defects are much easier to form in surface than in bulk. Thus, point defects may first form in surface and then diffuse into bulk. In this way, the surface is supposed to play an important role in maintaining or recovering the equilibrium concentration of the point defects. On the other hand, the surface itself is technologically important. In experiments, many wurtzite ZnO films have polar surfaces, which indicates that the c axis (0001) is a natural growth orientation. The O-terminated (0001)-O surface was believed to exist in an unreconstructed, truncated-bulk-like state,[29] whereas the other surface is more complicated and excluded from this work. In this paper, we will investigate the diffusion behaviour of intrinsic surface point defects in the O-terminated (0001)-O surface, in which both in-plane and into-bulk processes are included.

2. Calculational method and models

Density functional calculations were carried out using the plane-wave based Vienna *ab initio* simulation package (VASP),[30,31] based on the generalized-gradient approximation (GGA) with the functional of Perdew, Burke, and Ernzerhof (PBE).[32] The electron wavefunctions were described using the projector augmented wave (PAW) method of Blöchl[33] in the implementation of Kresse and Joubert.[34] Plane waves have been included up to a cutoff energy of 400 eV. Electronic states were occupied with a Gaussian smearing width of 0.05 eV. A realspace projection scheme was used for efficient computation. Orthogonal supercells containing 120 atoms were employed (5 Zn–O layers plus 10 Å vacuum), with $a_1 = 11.40$ Å(1 Å=0.1 nm), $a_2 = 9.87$ Å, $a_3 = 21.23$ Å, see Fig. 1(a), therein atoms of layer 1, 2 and 3 are fixed to simulate the bulk environment. All calculations were carried out by using the theoretical constant of bulk wurtzite ZnO. For integration within the Brillouin zone specific k points were selected using $2 \times 2 \times 1$ 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.

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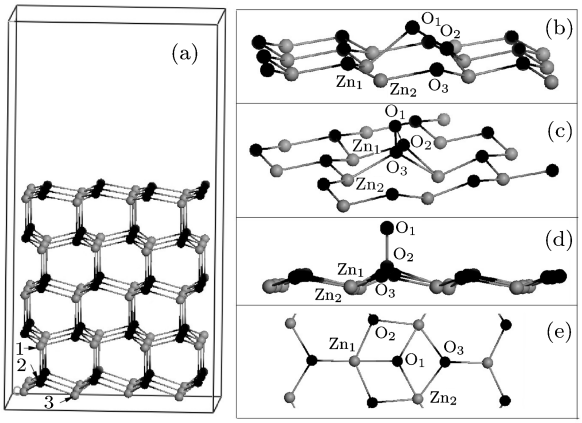


Fig. 1. Relevant atomic configurations. (a) Calculational model. Orthogonal suppercells containing 120 atoms, atoms of layers 1, 2 and 3 are fixed to simulate the bulk environment. (b) Oxygen dumbbell interstitial-like configuration. (c) Intermediate configuration of oxygen interstitial for diffusion in surface. (d) Intermediate configuration of oxygen interstitial for on-site diffusion for dumbbell interstitial-like configuration. (e) Unstable octahedral interstitial-like configuration.

In order to obtain the energy barriers for the various diffusion paths we employed the climbing image nudged elastic band method[35,36] as implemented in VASP by Henkelman, Jonsson, and others.[37] The images of the CI-NEB were relaxed until the maximum residual force was less than 0.01 eV/Å.

3. Results and discussion

3.1. O vacancy diffusion

First, we investigate oxygen vacancy diffusion in the surface, via exchange with the nearest neighbour oxygen atom in the surface. There is one intermediate state during the diffusion process, as shown in Fig. 2(a) (only one half of the migration path is shown, for symmetric consideration). This intermediate state is O_i–$2V_O$ complex as can be seen. The migration energy barrier is 0.94 eV, which is much smaller than the in-plane diffusion of bulk oxygen vacancy, 2.06 eV for the neutral state, 1.44 eV for the +2 charge state.[38] Second, we investigate oxygen vacancy diffusion from surface into bulk, via exchange with the nearest neighbour oxygen atom in bulk. The calculated energy along the migration path is shown in Fig. 2(b). We can see that the oxygen vacancy in the second layer from the surface has about 0.75 eV higher energy. It indicates that oxygen vacancy tends to locate in the surface. The migration energy barrier is 1.57 eV, smaller than 2.34 eV for the neutral state, and larger than 1.46 eV for the +2 charge state of the out-of-plane diffusion of bulk oxygen vacancy.[38] For surface defects, to date, it is not clear how to deal with the charge states properly,[39] therefore, we only consider the neutral charge state, though the charge state may have a large influence on the results, based on the bulk results.[20]

3.2. Zn vacancy diffusion

Similar to the O vacancy, there is one intermediate state during the diffusion process of the Zn vacancy in the surface, as shown in Fig. 2(c), which can be seen as a Zn_i–$2V_{Zn}$ complex. The migration energy barrier is 1.04 eV, which is similar to the bulk zinc vacancy diffusion, about 1 eV.[28] Then, we investigate zinc vacancy diffusion from surface to bulk. The calculated energy along the migration path is shown in Fig. 2(d). We can see that the zinc vacancy in the second layer from the surface has about 0.14 eV lower energy. It indicates that the zinc vacancy does not tend to locate in the the surface. The migration energy barrier is 0.68 eV, smaller than the bulk zinc vacancy diffusion ($\sim$ 1 eV).

3.3. O interstitial diffusion

The so-called O interstitial in the surface is actually one oxygen adatom in the surface. The atomic configuration of the O interstitial in the surface is more or less complicated. The most stable configuration is shown in Fig. 1(b). It can be seen that two oxygen atoms occupy one oxygen lattice site, similar to the oxygen split-interstitial or so-called dumbbell interstitial of the neutral charge state in bulk.[26,27,38] As shown in Fig. 2(e), there is one intermediate state of diffusion of the dumbbell interstitial in the surface, shown in Fig. 1(c). The energy barrier is 0.57 eV. In order to obtain long scale diffusion, the dumbbell interstitial must transform to another dumbbell interstitial on the same lattice site. One intermediate state is found, as shown in Fig. 1(d). This intermediate state has 0.11 eV higher energy than the dumbbell interstitial, with less than 0.1 eV energy barrier to relax to the dumbbell interstitial. That is to say, the on-site transformation has about 0.2 eV energy barrier. Next, we investigate the diffusion of the dumbbell interstitial into the second layer from the surface. The calculated energy along the migration path is shown in Fig. 2(f).

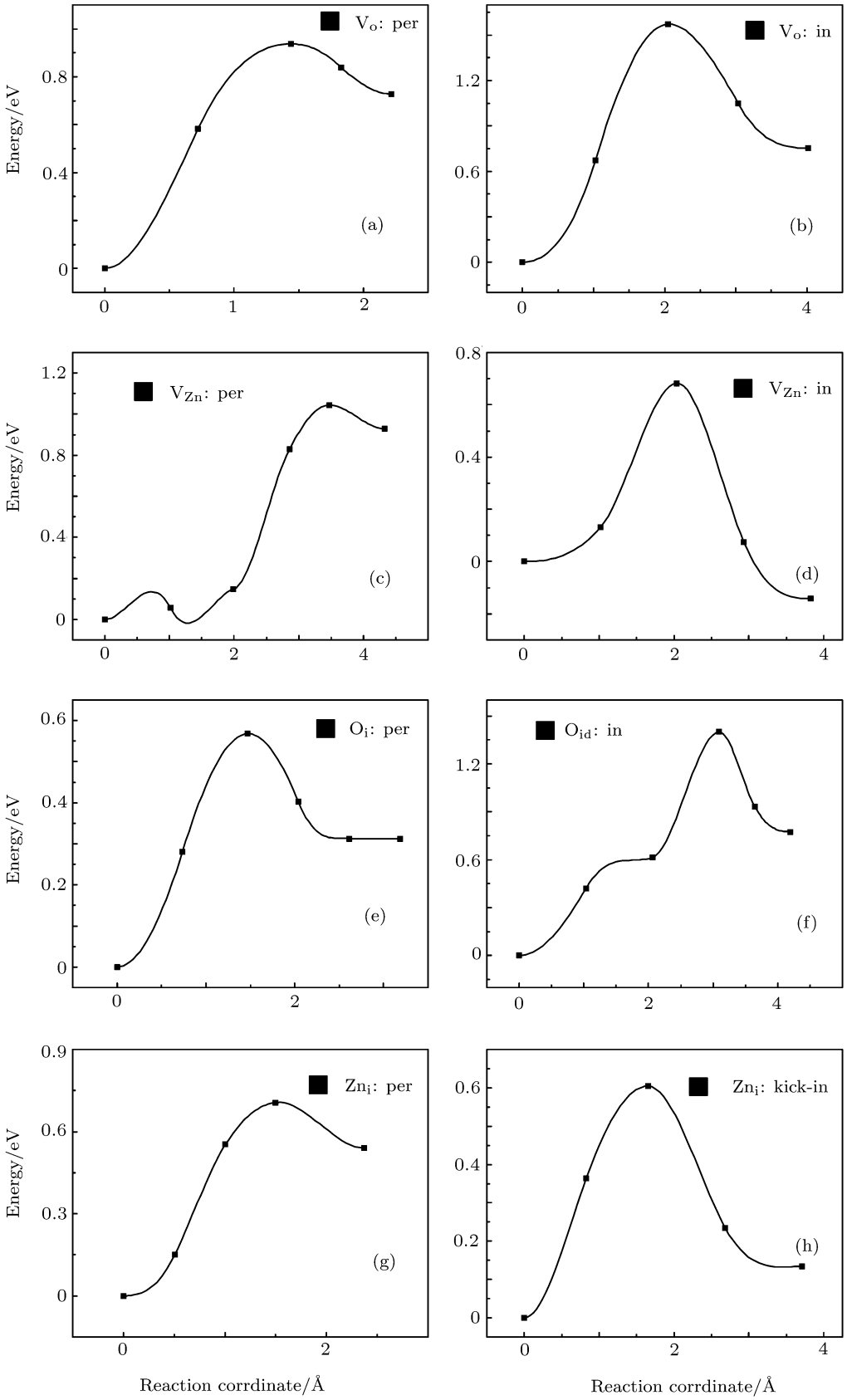


Fig. 2. Calculated energy along the migration paths. (a) O vacancy diffusion in surface. (b) O vacancy diffusion into bulk. (c) Zn vacancy diffusion in surface. (d) Zn vacancy diffusion into bulk. (e) O interstitial diffusion in surface. (f) O interstitial diffusion into bulk. (g) Zn interstitial diffusion in surface. (h) Zn interstitial diffusion into bulk.

We can see that the oxygen dumbbell interstitial in the second layer from the surface has about 0.76 eV higher energy. It indicates that the oxygen dumbbell interstitial tends to locate in the surface. The migration energy barrier is 1.40 eV, which is higher than the corresponding bulk diffusion (∼1 eV). Notice that we only investigate the neutral charge state here, but for other charge states, the oxygen interstitial may have a different stable configuration. It is known that for the −2 charge state in bulk, the oxygen interstitial tends to locate in the octahedral interstitial (in the centre of the hexagonal channel).[28] We check the configuration which corresponds to the octahedral interstitial, as shown in Fig. 1(e). We find that the octahedral interstitial-like configuration is very unstable, with 1.69 eV higher energy than the dumbbell interstitial. We also tried to simply add one, two or three electrons to the system, following the methods of bulk calculations, and expected the octahedral interstitial-like configuration to have a lower energy than the dumbbell interstitial-like configuration. However, the energy difference changes little. It seems that the charge state of the surface defect cannot be dealt with in the same way as bulk point defects, as suggested by Ref. [30]. We also check the configuration in which oxygen atom O_1 on top of zinc atom Zn_1, and find that it is not stable and easily relaxed to the dumbbell interstitial-like configuration (see Fig. 1(b)).

3.4. Zinc interstitial diffusion

Similar to the O interstitial, the so-called Zn interstitial in the surface is one zinc adatom in the surface. We find there is only one stable configuration for the Zn interstitial in the surface, which is the octahedral interstitial-like configuration, similar to the O octahedral interstitial-like configuration, shown in Fig. 1(e), substituting O_1 with Zn. First, we investigate Zn diffusion in the surface, where Zn goes through top of one nearest neighbour zinc atom. There is one intermediate state, in which zinc pushes the nearest neighbour zinc atom downwards to the tetrahedral interstitial site. The migration barrier is 0.71 eV. The calculated energy along the migration path is shown in Fig. 2(g). However, it is known that the tetrahedral interstitial site is highly unstable, and is easily relaxed to the octahedral interstitial site. We check the process to transform the tetrahedral interstitial into the octahedral interstitial, and find that there is an extremely small energy barrier, less than 0.1 eV. It indicates that, though the seemingly energy barrier is small for in-plane diffusion of the Zn interstitial, the Zn interstitial tends to be trapped and is not easy to diffuse directly in the surface. Furthermore, because the Zn interstitial is a very fast diffuser, after the Zn surface interstitial is trapped, the generated zinc octahedral interstitial is easy to diffuse away from the surface, and does not tend to kick the Zn interstitial back to the surface. So the Zn interstitial is difficult to diffuse in the surface. Next, we investigate the diffusion of the Zn interstitial into the second layer from the surface via the kick-out mechanism. The calculated energy along the migration path is shown in Fig. 2(h). We can see that the Zn interstitial in the second layer from the surface has about 0.13 eV higher energy. The migration barrier is relatively small, at 0.60 eV. It indicates that the Zn interstitial in the surface is not very stable, and not easy to move in the surface either. It is possible that the Zn interstitial is first kicked into the first layer from the surface, and then kicked back to the surface, as mentioned above. In such a way, it can diffuse in the surface with a relative small energy barrier, 0.73 eV. However, since the Zn interstitial is a fast diffuser in bulk ZnO, once it is kicked into the bulk, it can diffuse away from the surface with 0.4–0.5 eV energy barrier.[28] Thus, this does not happen easily. From our previous work,[28] we know that the direct diffusion along the c axis process has a similar but larger energy barrier than the kick-out process, so here we do not consider that the Zn interstitial diffuses directly along the c axis into the bulk.

All calculated energy barriers are summarized in Table 1.

Table 1. Calculated energy barriers for diffusion of point defects in O-terminated (0001) surface in wurzite ZnO.

migration path	energy barrier/eV
V_O: in-plane	0.94
V_O: into-bulk	1.57
V_{Zn}: in-plane	1.04
V_{Zn}: into-bulk	0.68
O_i: in-plane	0.57
O_i: into-bulk	1.40
Zn_i: in-plane	0.71
Zn_i: into-bulk	0.60

4. Conclusion

We have performed a detailed first-principles study of the diffusion behaviour of point defects in the

O-terminated (0001) surface in wurtzite ZnO. The O vacancy is found to diffuse much more easily in the surface than in bulk, with a 0.94 eV energy barrier, but it is not easy to diffuse into the bulk, with a 1.57 eV energy barrier. The diffusion of the Zn vacancy in the surface is similar to the bulk diffusion, with a 1.04 eV energy barrier, whereas it is relatively easy to diffuse into bulk, with a 0.68 eV energy barrier. The O interstitial can diffuse much more easily in the surface than in bulk, with only a 0.57 eV energy barrier, whereas it is not easy to diffuse into bulk, with a 1.40 eV energy barrier. The Zn interstitial is difficult to diffuse in the surface directly because of trapping effects, but it is relatively easy to diffuse into bulk, with a 0.6 eV energy barrier. The diffusion behaviour of point defects in the surface is essential for understanding surface physics.

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