**Diffusion Mechanisms of Ag atom in ZnO crystal: A First Principles Study**

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**Abstract.** Zinc oxide (ZnO) is currently under intensive investigation, as a result of its various applications in micro, nano and optoelectronics. However, a stable and reproducible p-type doping of ZnO is still a main challenging issue. Group IB elements such as Au, Cu and Ag, are promising candidates for p-type doping. Particularly, Ag atoms has been shown to be able to easily diffuse through the crystal structure of ZnO and lead to the p-type doping of the host crystal. However, the current understanding of Ag defects and their mobility in the ZnO crystal is still not fully explored. In this work, we report the results of our first-principles calculations based on density functional theory for Ag defects, particularly the interstitial and substitutional defects in ZnO crystal. Defect formation energies are calculated in different charged states as a function of Fermi energy in order to clarify the p-type behaviour of Ag-doped ZnO. We also investigate the diffusion behaviour and migration paths of Ag in ZnO crystal in the framework of density functional theory applying climbing image (CI) nudged elastic band method (NEB).

**Keywords:** Density functional theory, First-principles, ZnO, P-type, Ag doping, Formation energy, Diffusion barrier, Nudged elastic band.

**1. Introduction**

Different aspects of oxide semiconductors, owing to their wide and direct energy band gaps and considerable chemical stability at high temperatures and harsh environments are being considered for many electronic applications [1-3]. The main shortcoming of these oxides in this field is the fact that their p-type alternatives have remained elusive [4]. The wurtzite-ZnO, with a wide band gap (3.4 eV) and large exciton binding energy (60 meV), has been considered as an interesting material in wide range of applications in micro, nano and optoelectronics, as well as sensors technology and energy conversion system [5]. ZnO generally shows n-type behavior due to high concentration of oxygen vacancies in fabricated samples. However, in different applications such as light emitting diode (LED) and laser devices having a p-type ZnO is also necessary. Therefore, the fabrication and characterization of p-type ZnO has been the subject of many recent experimental and theoretical works [6].

In spite of many effort to obtain high mobility and high quality low resistance p-type ZnO, they have not been successful except in specific conditions in theoretical and experimental works [7, 8]. The common studied dopants are group-V atom (N, P and As) and group-I atom (Li, Na, K, Au, Cu and Ag) which substitute on the O and Zn sites in ZnO crystal lattice, respectively [9, 10]. However, there are
differences and discrepancies among theoretical and experimental results and a general understanding has not yet been achieved. One of the dopant elements which recently has attracted attentions is Ag, which is promising for the achievement of high quality and stable p-type ZnO [11]. The diffusion and stability properties of Ag dopant in ZnO crystal structure, particularly Ag interstitial defect, are very important in order to reach a comprehensive understanding of the p-type behavior of Ag-doped ZnO [12].

In this work, we report the results of our first-principles calculations based on density functional theory for Ag defects, particularly the interstitial defect (Agi) in ZnO crystal structure. Four configurations of Agi are considered in ZnO crystal structure. The defect formation energy is calculated in different charged states as a function of the Fermi energy in order to determine the most stable site of Ag interstitial defects. We also investigate the diffusion behavior and migration paths of Ag in ZnO crystal in the framework of density functional theory applying climbing image (CI) nudged elastic band method (NEB).

2. Calculation Method

Density functional calculations were carried out using the plane-wave-based Quantum Espresso code [13], based on generalized-gradient approximation (GGA) with the functional of Perdew, Burke and Ernzerhof (PBE) [14]. Norm conserving pseudopotentials were used for all elements considering the 3d104s2, 2s2p6 and 4d105s1 electronic configuration for Zn, O and Ag atoms, respectively. A cutoff energy of 70 Ry was used for real space sampling, whereas the Brillouin zone was sampled with a 6x6x3 k-point grid for ZnO unit cell. It has been shown that a large 3x3x2 supercell with 72 atoms is required to reduce the interaction between defects with their images in the neighbor cells. Thus, the defect calculations were performed in a 3x3x2 supercell with a 2x2x2 k-point sampling. The convergence threshold on all forces is 10^-6 in relax calculation. The calculated lattice parameters of ZnO are, a=3.3088 Å, c/a=1.6123 and Zn-O=2.021 Å in good agreement with the experimental values of a=3.25 Å, c/a=1.60 and Zn-O=1.97 Å [15].

The required energy to generate a defect in the perfect lattice is introduced as defect formation energy. The Ag interstitial defects are constructed by adding an Ag atom in the 3x3x2 ZnO supercell. The formation energy was calculated from the following equation:

\[ E_{\text{Formation}} = E_{\text{Total}}^{\text{Defect}} - \left[ E_{\text{Total}}^{\text{Perfect}} \pm \sum_i \mu_i \right] + q(\varepsilon_V + E_F) \]  

(1)

Where \( E_{\text{Total}}^{\text{Perfect}} \) and \( E_{\text{Total}}^{\text{Defect}} \) are the total energies of perfect and defected supercells, \( \mu_i \) is the chemical potential of removed or added elements. \( q \) is the fundamental electron charge, \( \varepsilon_V \) is the energy of the valence band edge and \( E_F \) is the Fermi energy which could vary between the valence and conduction band edges. The climbing image nudged elastic band method (CI-NEB) [16], as implemented in quantum espresso is used to calculate the energy barrier for Agi diffusion path. The images of the CI-NEB were relaxed until the maximum residual force was less than 0.001 eVÅ^-1.

3. Results

3.1. Structural configurations of Ag interstitial

The relaxed ZnO supercell structure with 72 atom is shown in figure 1.a. Four different configurations of Agi defects are considered to determine the most energetic stable one in ZnO crystal structure. The relaxed supercell structure of the interstitial defects are depicted in figure 1.b-e. These structures show the deformation around the interstitial Ag atom.
Figure 1. (a) The wurtzite structure of ZnO $3 \times 3 \times 2$ supercell, (b) configuration-1 of Ag$_i$, (c) configuration-2 of Ag$_i$, (d) configuration-3 of Ag$_i$, (d) configuration-4 of Ag$_i$.

3.2. Ag interstitial formation energy

The formation energy of defects which are demonstrated in figure 1 are calculated based on equation (1). The formation energies in neutral and charged state are shown in figure 2 as a function of the Fermi energy. Among the different configurations the (d) configuration shows the lowest formation energy and therefore could be considered as the most probable interstitial site for Ag atoms.

Figure 2. The calculated formation energy of Ag$_i$ for different configurations. Configuration-1 (Ag$_i$ (b)), configuration-2 (Ag$_i$ (c)), configuration-3 (Ag$_i$ (d)), configuration-4 (Ag$_i$ (e)).
3.3. Ag interstitial diffusion

Although the Ag ion has been considered as an extremely mobile dopant in metal oxide semiconductor [17, 18] as well as ZnO crystal structure, understanding the diffusion mechanisms of Ag dopant is very important to find out the p-type behavior of ZnO. In this work, we investigate the diffusion behavior of neutral Ag atoms through a minimum energy path perpendicular to the c axes of ZnO crystal structure. We calculated the energy barrier, which an interstitial Ag atoms have to overcome in order to move through the crystal structure. The diffusion path of Ag interstitial is illustrated in figure 3. The calculated energy along this diffusion path is shown in figure 4. It is obvious that the highest energy barrier of this diffusion path is 0.36 eV which is in good agreement with previous work [12]. The calculated diffusion barrier shows that this defect can easily diffuse in ZnO lattice. These results indicate that high quality p-type ZnO could be possibly fabricated by implantation or diffusion doping of Ag atoms.

Figure 3. Diffusion path of Ag, perpendicular to the c axes of ZnO crystal structure in four Image.
(a) Image 1, (b) Image 2, (c) Image 3, (d) Image 4.
4. Conclusion

We report the results of our first-principles calculations based on density functional theory for Ag defect, particularly the interstitial defect (Ag\textsuperscript{i}) in ZnO crystal structure. Four configurations of Ag\textsuperscript{i} are considered in ZnO crystal structure and defects formation energies are calculated in neutral and charged states as a function of the Fermi energy in order to determine the most stable site of Ag interstitial defects. The results show that the (d) configuration with a formation energy of 2.4 eV is the most stable one. The calculated diffusion barrier for this stable Ag\textsuperscript{i} defect perpendicular to the c axis of ZnO crystal is 0.36 eV in good agreement with the previous work [12]. This low energy barrier could lead to an easy diffusion of Ag dopant in ZnO lattice, which in turn could pave the way for fabricating p-type ZnO.

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