



# In assisted realization of p-type C-doped ZnO: A first-principles study

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## ABSTRACT

C mono-doped and C–In co-doped ZnO are investigated by the first-principles calculations. It is found that the C mono-doped ZnO is p-type with hole carriers locating nearby valence band maximum. Furthermore, a shallower C acceptor energy level appears in the band gap after incorporating In into C-doped ZnO system. Meantime, compared with C mono-doped ZnO, C–In co-doped ZnO has a lower formation energy, correspondingly a higher chemical stability, and thus to enhance the incorporation efficiency of C. These results suggest that C–In co-doping method provided an efficient technique for realizing p-type ZnO.

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## 1. Introduction

ZnO has attracted much attention because it has some interesting physical properties suitable for short wavelength optoelectronic device applications, such as blue and ultraviolet (UV) lasers, light-emitting diodes, and solar cells [1–3]. ZnO has a wide band gap (3.3 eV at room temperature) and lattice constants that are similar to those of GaN, which, together with AlGaIn and GaInN, currently are key materials for blue and UV photonics [4]. The exciton binding energy of ZnO is 60 meV, much larger than that of GaN (25 meV). Therefore, it is expected that a ZnO-based light emitter should be much brighter than a corresponding GaN light emitter. Furthermore, its low material cost, high crystalline quality, and high radiation resistance make it a promising material to compete with GaN-based technologies [5]. However, similar to most oxide materials, ZnO is more difficult to dope p-type than the nitride [6–8]. This is because oxygen is more electronegative than N, therefore, ZnO has a lower valence-band maximum than GaN. Consequently, acceptor levels are deep in ZnO, it will be much more difficult to dope ZnO p-type than to dope GaN p-type. The p-type doping bottleneck has so far behind the full utilization of ZnO as a novel optoelectronic material [4].

In the past decades, most of the investigations were focused on the mono acceptor doping technology such as Li [9], N [10], P [11], As [12] and Sb [13]. Theoretically, group-I element substituting on Zn sites is shallow acceptors, but instead these dopants tend to occupy the interstitial sites, partly due to their small atomic radius, and therefore act mainly as donors. Of the group-V elements, it has

been proposed that N is the most suitable dopant because it has about the same ionic radius as O, and thus should readily substitute on O sites. Indeed, it remains difficult to achieve good quality p-type conduction in N-doped ZnO either due to a low dopant solubility or a high defect ionization energy. The p-type conduction of ZnO has also been realized experimentally or theoretically by doping C [14–18]. The co-doping method could be another approach to improve and control conductivity. Co-doping schemes include Ga–N [19], Al–N [20], In–N [20], Li–F [22], Li–N [23], Te–N [N] [24], Be–N [25] and Mg–N [26].

In this work, C mono-doping and C–In co-doping in ZnO are studied by first-principles calculations, and it is found that C–In could be better dopants for p-type ZnO.

## 2. Details and calculations

We have performed calculations using the density functional theory, as implemented in CASTEP code [27], with the generalized gradient approximation of Perdew et al. [28] and ultrasoft pseudopotentials [29]. The valence-electron configurations for the O, Zn, C and In atoms are employed as  $2s^2 2p^4$ ,  $3d^{10} 4s^2$ ,  $2s^2 sp^2$  and  $4d^{10} 5s^2 5p^1$ , respectively. The cutoff energy for the plan-wave expansion is 340 eV. A 16 atoms supercell, which consists of  $2 \times 2 \times 2$  primitive wurtzite cells is used for calculations. The crystal structure of supercell is shown in Fig. 1. We use Monkhorst-Pack  $4 \times 4 \times 2$   $k$ -point mesh for Brillouin zone integration [30]. During calculations, all atoms of the supercell are allowed to relax until the Hellmann–Feynman forces acting on them become less than 0.03 eV/Å. The geometric structures of pure ZnO,  $Zn_{16}O_{15}C$  and  $Zn_{15}InO_{15}C$  systems are optimized. Band structure, the density of states (DOS) and Mulliken overlap

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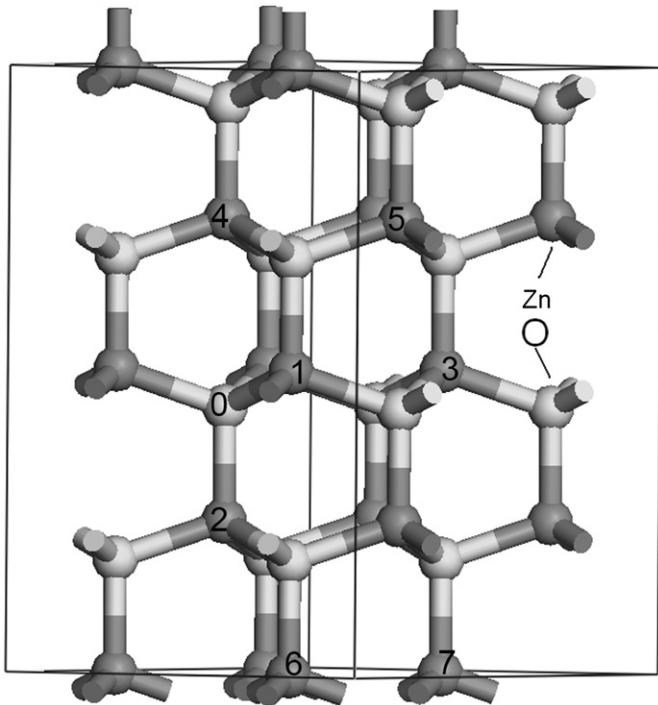


Fig. 1. The supercell structure for ZnO ( $2 \times 2 \times 2$ ). C site is labeled 0, and In sites are labeled 1–7.

Table 1

Relative energies of seven different configurations for C–In co-doped system. The numbers in brackets are responding to the numbers in Fig. 1. Configuration II has the lowest total energy, and the value of the total energy is defined as 0.000. The relative energy of the other configurations is given.

Configurations	I (0, 1)	II (0, 2)	III (0, 3)	IV (0, 4)	V (0, 5)	VI (0, 6)	VII (0, 6)
Total energy (eV)	0.172	0.000	0.375	0.307	0.596	0.525	0.588

populations are computed after the geometry optimization. Additionally, for C–In co-doped system, we have taken seven configurations into consideration. Relative energies are shown in Table 1. The configuration II has the lowest total energy. So we can infer that this configuration also has the lowest formation energy among all the configurations. Then, the discussion of electronic structure and properties is based on this configuration.

### 3. Results and discussions

#### 3.1. Geometric structure

The structural optimization is first performed for pure wurtzite ZnO. The optimized lattice parameters are  $a = 3.289 \text{ \AA}$  and  $c/a = 1.614$ , which agree with the experimental values of  $a = 3.250 \text{ \AA}$ ,  $c/a = 1.6021$  and other theoretical results [31,32].

The optimized lattice parameters and total energy for different structures are listed in Table 2. The calculated lattice parameters of doped ZnO mainly depend on the kinds of dopants as well as the sites replaced by the dopants.

Compared with pure ZnO, the value of  $c/a$  of  $\text{Zn}_{16}\text{O}_{15}\text{C}$  and  $\text{Zn}_{15}\text{InO}_{15}\text{C}$  increases. With respect to the Zn–O bond in pure ZnO, the bond length of C–Zn in the  $c$ -axis and un- $c$ -axis direction of  $\text{Zn}_{16}\text{O}_{15}\text{C}$  decreases and increases, respectively. The bond length of C–Zn in  $\text{Zn}_{15}\text{InO}_{15}\text{C}$  system is shorter than that of  $\text{Zn}_{16}\text{O}_{15}\text{C}$ ,

Table 2  
Optimized lattice parameters and total energy.

System	ZnO	$\text{Zn}_{16}\text{O}_{15}\text{C}$	$\text{Zn}_{15}\text{InO}_{15}\text{C}$		
Bond	Zn–O	C–Zn	In–O	In–C	C–Zn
Bond length ( $\text{\AA}$ )					
$c$ -axis	2.013	1.962	2.128		
Un- $c$ -axis	2.004	2.005	2.164		1.980
$a$ ( $\text{\AA}$ )	3.289	3.275	3.314		
$c/a$	1.614	1.638	1.621		
Total energy (eV)	–34,356.412	–34,069.560	–33,920.924		
Volume ( $\text{\AA}^3$ )	49.743	49.902	51.055		

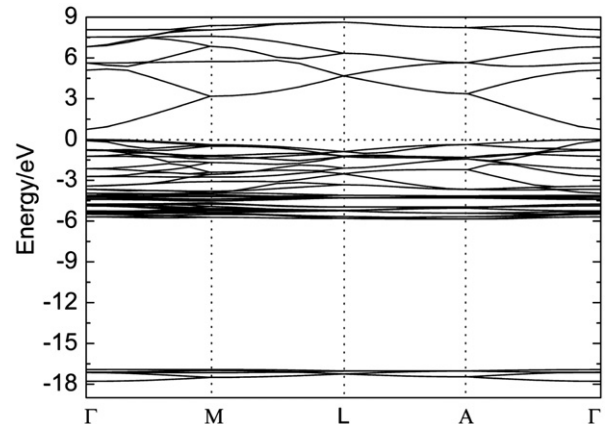


Fig. 2. The energy band structure of pure ZnO.

indicating strong overlap between C 2p and Zn 3d orbitals, which is consistent with the analysis in 3.5. The value of  $a$  of  $\text{Zn}_{16}\text{O}_{15}\text{C}$  is smaller than that of pure ZnO. Doped systems also have higher total energy. The volume of  $\text{Zn}_{16}\text{O}_{15}\text{C}$  increases slightly because the covalent radius of C (0.77  $\text{\AA}$ ) is larger than that of O (0.73  $\text{\AA}$ ).  $\text{Zn}_{15}\text{InO}_{15}\text{C}$  has the largest volume because the covalent radius of In (1.44  $\text{\AA}$ ) is larger than that of Zn (1.25  $\text{\AA}$ ).

#### 3.2. Formation energy

To check the energy stability for doped ZnO, we calculate corresponding formation energy which is expressed as

$$E_f = E_{\text{tot}} - E_{\text{ref}} - mE_C - nE_{\text{In}} + mE_O + nE_{\text{Zn}}, \quad (1)$$

where  $E_{\text{tot}}$ ,  $E_{\text{ref}}$ ,  $E_C$ ,  $E_{\text{In}}$ ,  $E_O$  and  $E_{\text{Zn}}$  are the energy of doped ZnO, pure ZnO, an isolated carbon atom, a In atom in bulk In, an O atom in the oxygen molecule and a Zn atom in bulk Zn, respectively [33]. The integers  $m$  and  $n$  are the numbers of C and In atoms which substitute O and Zn, respectively. The formation energy of  $\text{Zn}_{16}\text{O}_{15}\text{C}$  and  $\text{Zn}_{15}\text{InO}_{15}\text{C}$  systems is calculated to be 1.318 and  $-1.756 \text{ eV}$ , respectively, indicating C–In co-doped ZnO has a higher chemical stability.

#### 3.3. Electronic structure of ZnO

Fig. 2 shows the energy band structure of pure ZnO. The direct band gap is 0.746 eV at a highly symmetric G point, which is in good agreement with other theoretical calculations [34–36], but much less than the experimental one, 3.4 eV. This underestimation is due to the well-known limitation of DFT calculations [37]. The lower valence band from mainly Zn 3d changes slowly because the 3d states of Zn are full of electrons. And the gentle change of the upper valence from the O 2p compared with the

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