First-principle study on the effect of high Ag–2N co-doping on the conductivity of ZnO

WENXUE ZHANG¹, YUXING BAI¹, CHENG HE^{2,*} and XIAOLEI WU¹

¹School of Materials Science and Engineering, Chang'an University, Xi'an 710064, China

²State Key Laboratory for Mechanical Behavior of Materials, School of Materials Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China

MS received 10 January 2014; revised 27 June 2014

Abstract. The geometric structure, band structure (BS) and density of state (DOS) of pure and p-type co-doping wurtzite ZnO have been investigated by the first-principle ultrasoft pseudopotential method with the generalized gradient approximation. These structures induce fully occupied defect states above the valence-band maximum of doped ZnO. The calculation results show that in the range of high doping concentration, when the co-doping concentration is more than a certain value, the conductivity decreased with the increase of co-doping concentration of Ag–2N in ZnO. Our findings suggest that co-doping of Ag–2N could efficiently enhance the N dopant solubility and is likely to yield better p-type conductivity.

Keywords. First-principle; ultrasoft pseudopotential method; p-type conductivity.

1. Introduction

Zinc oxide is a promising optoelectronic material, which can be used for blue and ultraviolet light-emitting diodes, laser diodes and solar cells due to its wide band gap of 3.2 eV.^{1,2} It has been suggested that undoped ZnO is n type due to a large number of intrinsic defects such as oxygen vacancies (V_O) and Zn interstitials (Zn_i).³ p-type doping of ZnO has attracted great attention, because of its potential application for next-generation short-wavelength optoelectronic devices.^{4–9} The obstacle that prevents full usage of ZnO as a novel optoelectronic material is the inability of obtaining p-type conductivity with high hole concentration and low resistivity. Therefore, many efforts have been made to achieve p-type ZnO, with using many techniques and dopants. For example, group-V elements (N, P, As and Sb) on O sites such as N were used as popular p-type dopants.^{10–13} Although, several experiments were successful in achieving p-type ZnO doped with N impurities,^{11–13} sufficient high-quality p-type ZnO with low resistivity and high mobility has not been achieved yet either due to a low dopant solubility or a high defect ionization energy.¹⁴

Moreover, theoretical studies indicated that the acceptor level of N is so deep that it is difficult to explain the activity of N acceptors at room temperature.¹⁵ Group-I elements such as Li and Na on substitutional Zn sites, are also acceptor candidates. However, with smaller ionic radii, Li or Na tends to occupy the interstitial site rather than substitutional sites, which leads to the self-compensation.¹⁵ In contrast, group IB elements (Cu, Ag and Au) have suitable size for substitution

of Zn. Ag-doped p-type ZnO has been successfully achieved in the experiment.¹⁶ Yan *et al.*⁴ and Wan *et al.*¹⁵ found that the transition energies $E(0/-)$ for Ag_{Zn} are relatively high at 0.4 eV above the valence-band maximum (VBM), thus Ag_{Zn} is expected to induce a deep acceptor level.^{4,15} Therefore, p-type ZnO is difficult to be gained in Ag-doped ZnO. A recent experiment showed that Ag and N co-doping has produced the best codoped p-type ZnO.¹² In order to understand the doping mechanism and the acceptor levels of this dual-acceptor co-doped ZnO, further theoretical studies are required in addition to the available experimental work.

In this work, we investigate a theoretical study to understand the effect of high Ag–2N co-doping on the conductivity of ZnO by using density-functional theory (DFT). The formation energy, ionization energy, atomic structure and electronic structure properties of Ag–2N-codoped ZnO are calculated.

2. Computational details

The simulation is calculated by first-principle DFT, which is provided by DMOL³.^{16–18} The generalized gradient approximation (GGA) of Perdew and Wang (GGA-PW91) is employed to optimize geometrical structures and calculate properties.¹⁹ The all-electron relativistic Kohn–Sham wave functions are expanded in the local atomic orbital basis set.¹⁶ The valence-electron configurations are: Zn-3d¹⁰4s², O-2s²2p⁴, N-2s²2p³, Ag-4d¹⁰5s¹. The k -point is set to $4 \times 4 \times 2$ for all structures, which brings out the convergence tolerance of energy of 1.0×10^{-5} Ha (1 Ha = 27.2114 eV), maximum force of $0.002 \text{ Ha } \text{\AA}^{-1}$ and maximum displacement of $0.005 \text{ \AA}$.

* Author for correspondence (hecheng@mail.xjtu.edu.cn)

The electronic distributions of ZnO are carried out by the Mulliken charge analysis, which is performed using a projection of a Linear Combination of Atomic Orbitals (LCAO) basis and to specify quantities such as atomic charge, bond population, charge transfer, etc. LCAO supplies better information regarding the localization of the electrons in different atomic layers than a plane wave basis set.²⁰ The obtained relative values of the charge e , but not the absolute magnitude, display a high degree of sensitivity to the atomic basis set and a relative distribution of charge with which e is determined.^{21,22}

The ground state of a ZnO crystal has a wurtzite structure (space group P6₃mc) with two zinc and two oxygen atoms per unit cell. The $2 \times 2 \times 2$ supercell of pure ZnO employed contained 32 atoms. The calculated lattice parameters for ZnO are $a = 3.249 \text{ \AA}$ and $c/a = 1.602$, in good agreement with the measured values.¹⁵ The $2 \times 2 \times 2$ supercell of $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ (figure 1a) and $3 \times 2 \times 1$ supercell of $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$ (figure 1b) are modelled by substituting one Ag on a Zn site (Ag_{Zn}), one N for the O site (N_{O}) located at the nearest-neighbour site of Ag atom and substituting a second N atom the O atom located at the next nearest-neighbour site of Ag atom.

To determine whether it is energetically preferred that two dopants bind, e.g., Ag_{Zn} and N_{O} , in the neutral charge state, we calculate the binding energy which is defined as

$$E_{\text{b}}(\text{ZnO} : \text{Ag}-2\text{N}) = E_{\text{tot}}(\text{ZnO} : \text{Ag}-2\text{N}) + E_{\text{tot}}(\text{ZnO}) - E_{\text{tot}}(\text{ZnO} : \text{N}) - E_{\text{tot}}(\text{ZnO} : \text{Ag}), \quad (1)$$

where $E_{\text{tot}}(\text{ZnO} : \text{Ag}-2\text{N})$, $E_{\text{tot}}(\text{ZnO} : \text{N})$ and $E_{\text{tot}}(\text{ZnO} : \text{Ag})$ are the total energies for supercells containing defects $\text{Ag}_{\text{Zn}}\text{N}_{\text{O}}$, N_{O} and Ag_{Zn} , respectively. A negative value of E_{b} corresponds to a metastable or a stable bound dopant pair when both are present in the system. According the equation,

in the above case, the system energy is the lowest, and the structure is the most stable.²³ The co-doping concentration of Ag-2N in $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ is 9.375 at%, while in $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$ is 12.5 at%. As the doping mode is substitution doping, the symmetry is not changed and $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ and $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$ are isomorphic to the pure ZnO.²⁴

3. Results and discussion

3.1 Geometry optimization results

The wurtzite structures of pure ZnO, $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ and $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$ are optimized when Ag was on the Zn site (Ag_{Zn}) and N on the O site, N_{O} . The optimized geometry parameters are in good agreement with experimental results,²⁵ which indicate that the geometry parameters in the paper are reliable. The electronic distributions in pure ZnO is analysed by the Mulliken charge analysis.²⁶ The results indicate that the same atoms are equivalent and $e_{\text{zn}} = 0.873$ and $e_{\text{O}} = -0.873$ in charge transfer. In addition, considering the symmetry, stability and computing speed, the substitution location is as close as possible to the centre position.

The lattice parameters a and c/a of updoped ZnO are larger than those of the doped ZnO. And the bond lengths become also longer at the same direction. The radius of Ag^+ (1.26 Å) is longer than that of Zn^{2+} (0.74 Å) when Ag is on the Zn site. The ionic radius of N^{2-} (1.46 Å) and covalent radius of N (0.75 Å) are both longer than those of O^{2-} (1.32 Å) and O (0.66 Å). But the proportion of the covalent bond to the chemical bond is larger for the N-Zn bond than for the O-Zn bond according to population analysis,²⁸ which is consistent with experimental results. It is illuminated that the volume of ZnO is swelled after Ag, N doping in ZnO and the difference of the radii between the dopant cation and the host ions.

Figure 1. Supercell of (a) $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ and (b) $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$.

3.2 Doping concentration

When the order of magnitude of doping concentration is less than 10^{18} cm^{-3} , the doped semiconductor is considered to be below doping. In this case, the doping concentration has almost no effect on the mobility, and the mobility is assumed to be constant. While the order of magnitude is greater than or equal to 10^{18} cm^{-3} , the doped semiconductor is considered to be highly doped. In this case, the doping concentration has greater effect on the mobility, and the mobility is variable.²⁴ In the paper, after geometry optimization, the calculated values of dopant concentration are 1.71×10^{21} and $2.28 \times 10^{21} \text{ cm}^{-3}$ for $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ and $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$, respectively. Hence, both of them are high doping.

3.3 Conductivity

The conductivity ratios of $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ and $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$ are calculated to identify promising candidates for p-type ZnO doping. The numbers of holes of various structures are calculated by integrating the areas from the Fermi level to the VBM.

Comparing with the electronic structure of doped ZnO semiconductor, DOS and band structure of the undoped ZnO are firstly calculated after geometry optimization. The calculated results are shown in figure 2. Figure 2a shows the calculated band structure of the undoped ZnO. It shows that ZnO has a direct band gap, which is 0.917 eV smaller than the experimental result 3.3 eV.¹ That the electronic band gaps of semiconductors result grossly underestimated is a well-known artifact of the traditional DFT.¹⁵ Moreover, our calculated band structure is in agreement with the other calculated results.²⁷ In figure 2, the Fermi level of pure ZnO is at the top of the valence band (VB). In this paper, the Fermi level has been specified to be 0 eV.²⁴ The partial density of states of O-2s, O-2p, Zn-4s and Zn-3d orbitals are labelled. There are four groups of peaks in DOS of the undoped ZnO. The lowest band ranges from -19 to -15 eV and corresponds to

Figure 2. (a) Band structure (BS) and (b) PDOS of pure ZnO.

the core states consisting of mainly O-2s and Zn-3d orbits. This narrow valence band region is not discussed because of its weak interaction with other electron states. The lower valence band (-6.50 to -4.40 eV) consists of a mixture of Zn-3d and O-2p states. The upper valence band (-4.40 to -0.20 eV) is mainly composed of O-2p states with a small contribution from Zn-3d states. The upper valence band from the O-2p illustrates that the holes in the valence band have a biggish effective mass, which is one of the main reasons for the difficulty in realization of p-type ZnO.¹⁵ The highest band above 0 eV denotes the conduction band (CB) consisting of primarily hybridized Zn-4s and O-2p orbits. Thus, E_g of undoped ZnO is essentially determined by Zn-4s and O-2p orbits, while the Zn-3d orbit plays an auxiliary effect.

The results of total DOS, PDOS and the band structure of $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ and $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$ are shown in figures 3 and 4, respectively. In figures 3 and 4, a strong localized energy band located at approximately -13 eV, which comes from N-2s state according to comparison with pure ZnO. N_O acts as an acceptor, inducing a defect state with a hole above the valence band, which originate mainly from N-2p with a little O-2p effect. The orbital energy of O-2p states shifts to a higher energy value because N is easier to obtain electrons from the neighbouring O atoms and the common movement is strengthened for the orbital hybridization effect occurring among O-2p states on N sites. The conduction band still consists mainly of O-2p states and Zn-4s states.

Compared with pure ZnO, there are still contributions from Ag-4d states and N-2p states besides O-2p states in VBM, and there are little contributions from the Ag-5s states besides the Zn-4s states in the conduction band maximum (CBM).

In figures 3 and 4, a new occupied band is recognized near the top of the valence band of AgZn-N_O , which is plotted by arrow. These can be regarded as a defect state induced by AgZn-N_O . From figures 3 and 4, we can see that the Fermi levels of both $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ and $\text{Zn}_{0.9167}$

Figure 3. (a) Band structure (BS) and (b) PDOS of $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$.

Figure 4. (a) Band structure (BS) and (b) PDOS of $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$.

$\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$ shifted downward into VB, which shows that both of them are high doping p-type degenerate semiconductors. Comparing figure 3 with figure 4, the degree of the Fermi surface shifting downward into the VB is different, which indicates that the relative hole number is different with different co-doping concentrations of Ag–2N in ZnO. This shows that the holes are not limited to N and Ag, but act on their neighbouring Zn and O atoms. There are two reasons for the results. The first is that the common movement of electrons from the N-2p states and Zn-4d states becomes stronger; the second is that there is a stronger orbital hybridization interaction between the O-2p states and of Ag-4d states. The calculated numbers of holes were 2.93 and 3.56 for $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ and $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$, respectively, according to the DOS being integrated from the Fermi level to the valence band maximum (VBM). And the values of total DOS are 287.06 and 288.32, respectively, which are obtained by integration over the whole valence band. The higher value of integral DOS confirms that there are more carriers provided by the $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$ and is helpful to form p-type ZnO by co-doping of N and Ag. It can be seen that with the increase of dopant concentration the number of holes in the valence band also increase.

The band gap reduces to 0.47 and 0.72 eV for $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ and $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$ compared with the pure ZnO, due to that VBM shifts to the higher energy region and CBM moves into the lower one. The band gap of $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ is the narrowest and its red-shift phenomenon is the most obvious one among the three configurations. The carrier concentration is increased, the electrical resistivity is reduced and the conductivity is improved for wurtzite ZnO codoped by N and Ag.

The doping concentration is related with scattering by ionized impurities based on first-principle studies. The scattering probability by the ionized impurities in doped semiconductor is increased with the doping concentration.^{24,29} Let N_i be the doping concentration, P_i be the scattering

probability by the ionized impurities and T be the thermodynamic temperature. The relationship among them is given by

$$P_i \propto N_i T^{-3/2}. \quad (2)$$

Again, the relaxation time τ_i is inversely proportional to P_i , so we have

$$\tau_i \propto N_i^{-1} T^{3/2}. \quad (3)$$

The hole conductivity can be expressed by

$$\sigma_i = P_i q^2 \tau_i / m_h^*, \quad (4)$$

where m_h^* is the hole effective mass and q the charge state. The hole effective mass m_h^* can be expressed by the following equation:

$$m_h^* = \hbar^2 (d^2 E / dk^2)^{-1}, \quad (5)$$

where $\hbar$ is the Planck constant, E the energy and k the wave vector. From equations (2) and (3), we can see that in the range of high doping concentration, the hole mobility μ_i is inversely proportional to the doping concentration N_i in doped semiconductor.

Let m_{h1}^* , m_{h2}^* be the hole effective mass corresponding to Γ point in figures 3 and 4, where the subscript 1 and 2 denote $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ and $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$, respectively. We got the second-order derivatives in the Γ direction of the curves at the top of VB in figures 3 and 4. Substituting these back into equation (5), we have $m_{h1}^* = 1.8887 \times 10^{-30}$ kg, $m_{h2}^* = 1.0731 \times 10^{-30}$ kg, thus, $m_{h1}^* < m_{h2}^*$. The calculation results show that in the range of high doping concentration, the higher the co-doping concentration of Ag–2N, the larger the hole effective mass in ZnO, which agrees with the above qualitative analysis results.

The hole conductivity of the $\text{Zn}_{0.9375}\text{Ag}_{0.0625}\text{O}_{0.875}\text{N}_{0.125}$ and $\text{Zn}_{0.9167}\text{Ag}_{0.0833}\text{O}_{0.8333}\text{N}_{0.1667}$ are set to be σ_1 and σ_2 , respectively. Based on the above analysis on the relative hole number and the hole mobility, in light of equation (4), the magnitude of σ_1 is 0.56 times of σ_2 . The calculation results show that in the range of high doping concentration, the higher the co-doping concentration of Ag–2N, the lower the hole conductivity in ZnO, which agrees with the above theoretical analysis results.

4. Conclusion

In summary, using the first-principle calculation of plane wave ultrasoft pseudopotential technology based on the DFT, we have investigated the geometry structure, electrical structure and conductivity of undoped and doped ZnO. The calculation results showed that in the range of high doping concentration, with the increase of co-doping concentration of Ag–2N the relative hole number shifting downward into the VB increases, the hole effective mass increases, and the hole conductivity decreases. In conclusion, the present results indicate that the carrier concentration is improved in N, Ag–co-doped ZnO, and this is helpful to form p-type ZnO.

Acknowledgements

We acknowledge supports by National Key Basic Research and Development Program (Grant nos 2010CB631001 and 2012CB619400), National Natural Science Foundation of China (NSFC, Grant nos 51101117 and 51301020), Ph.D. Programs Foundation of Ministry of Education of China (Grant no. 20110201120002), the Natural Science Basic Research Plan in Shaanxi Province of China (2011JQ6001) and the Fundamental Research Funds for the Central Universities and State Key Laboratory for Mechanical Behavior of Materials.

References

1. Lide D R (ed) 2007–2008 *CRC handbook of chemistry and physics* (Boca Raton, FL : CRC Press) 88th ed
2. Pearton S J, Norton D P, Ip K, Heo Y W and Steiner T 2004 *J. Vac. Sci. Technol. B* **22** 932
3. Zhang S B, Wei S-H and Zunger A 2001 *Phys. Rev. B* **63** 075205
4. Yan Y F, Al-Jassim M M and Wei S H 2006 *Appl. Phys. Lett.* **89** 181912
5. Vaithianathan V, Lee B T and Kim S S 2005 *Appl. Phys. Lett.* **86** 062101
6. Wang P, Chen N and Yin Z G 2006 *Appl. Phys. Lett.* **88** 152102
7. Kang H S, Ahn B D, Kim J H, Kim G H, Lim S H, Chang H W and Lee S Y 2006 *Appl. Phys. Lett.* **88** 202108
8. Park C H, Zhang S B and Wei S-H 2002 *Phys. Rev. B* **66** 073202
9. Wei S H 2004 *Comput. Mater. Sci.* **30** 337
10. Chen K, Fan G H, Zhang Y and Ding S F 2008 *Acta Phys. Chim. Sin.* **24** 61
11. Guo X L, Tabata H and Kawai T 2001 *J. Cryst. Growth* **223** 135
12. Zuo C Y, Wen J and Bai Y L 2010 *Chin. Phys. B* **19** 047101
13. Bian J M, Li X M and Zhang C Y 2004 *Appl. Phys. Lett.* **85** 4070
14. Duan X M, Stampfl C, Bilek M M M and McKenzie D R 2009 *Phys. Rev. B* **79** 235208
15. Wan Q X, Xiong Z H, Dai J N, Rao J P and Jiang F Y 2008 *Opt. Mater.* **30** 817
16. He H Y, Hu J and Pan B C 2009 *J. Chem. Phys.* **130** (c) 204516
17. Gelves G A, Lin B, Sundararaj U and Haber J A 2006 *Adv. Funct. Mater.* **16** 2423
18. Delley B 1990 *J. Chem. Phys.* **92** 508
19. Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
20. Davidson E R and Chakravorty S 1992 *Theor. Chim. Acta* **83** 319
21. Wang B L, Zhao J J, Chen X S, Shi D and Wang G H 2006 *Nanotechnology* **17** 3178
22. Segall M D, Shah R, Pickard C J and Payne M C 1996 *Phys. Rev. B* **54** 16317
23. Özgür Ü, Alivov Y I, Liu C, Teke A, Reshchikov M A, Doğan S, Avrutin V, Cho S J and Morkoc H 2005 *J. Appl. Phys.* **98** 041301
24. Hou Q Y, Li J J, Zhao C W, Ying C and Zhang Y 2011 *Physica B* **406** 1956
25. Abrahams S C and Bemstein J L 1969 *Acta Crystallogr. B* **25** 1233
26. He C, Qi L, Zhang W X and Pan H 2011 *Appl. Phys. Lett.* **99** 073105
27. Zuo C Y, Wen J and Bai Y L 2010 *Chin. Phys. B* **19** 047101
28. Vanderbilt D 1990 *Phys. Rev. B* **41** 7892
29. Huang K and Han N 1985 *Solid state physics* (Beijing : Higher Education Press)