Journal of Materials Science and Chemical Engineering, 2025, 13(11), 1-8
https://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

First-Principles Study on the Electronic and Optical Properties of Al- and F-Doped ZnO

Xiangjiang Xiao[1], Jinfu Wang[2], Decong Li[1], Kunyong Kang[3], Hanming Zhu[1*]

[1]School of Health and Nursing, Yunnan Open University, Kunming, China
[2]Huaning Yunengtou New Energy Development Co., Ltd., Yuxi, China
[3]School of Materials Science and Engineering, Southwest Forestry University, Kunming, China
Email: *hivdgzhm@163.com

How to cite this paper: Xiao, X.J., Wang, J.F., Li, D.C., Kang, K.Y. and Zhu, H.M. (2025) First-Principles Study on the Electronic and Optical Properties of Al- and F-Doped ZnO. *Journal of Materials Science and Chemical Engineering*, **13**, 1-8.
https://doi.org/10.4236/msce.2025.1311001

Received: October 16, 2025
Accepted: November 3, 2025
Published: November 6, 2025

Abstract

This study evaluated the electronic and optical properties of the Al- and F-doped ZnO by the first-principles study based on the density functional theory. The results show that the Al-3s, Al-3p, and F-2p orbitals introduce new impurity states near the Fermi level. This phenomenon significantly increases the density of states (DOS) in the conduction band of ZnO, which further enhances the carrier concentration and thus improves its electrical conductivity. It is worth noting that the electron mobility of F-doped ZnO is higher than that of Al-doped ZnO. Moreover, the two doped systems exhibit similar transmittance characteristics in the visible light band. This study provides a theoretical explanation for the modulation mechanisms of F and Al elements on the electronic structure and optoelectronic properties of ZnO.

Keywords

DFT, Al- and F-Doped ZnO, Electronic Structure, Optical Property

1. Introduction

Transparent Conductive Oxides (TCOs) are a category of special oxide materials that simultaneously possess high visible light transmittance, excellent electronic conductivity, and indispensable application value in the field of optoelectronics [1]. Indium tin oxide (ITO), which is indium trioxide (In_2O_3) doped with tin (Sn), is the most widely used TCO material at present [2]. However, this material has shortcomings such as high raw material cost, strict deposition process conditions, and weak mechanical properties, which limit its further application. Compared with ITO, ZnO thin films exhibit comparable optical and electrical properties. Specifically, they show characteristics including high visible light transmittance, a

wide band gap (3.37 eV), a large exciton binding energy, and high electron mobility. Meanwhile, ZnO also has advantages such as non-toxicity, low preparation cost, and abundant reserves of raw materials. Thus, it is expected to replace ITO as a promising candidate TCO material in the field of optoelectronics [3] [4].

However, single-component ZnO lacks chemical and thermal stability and has poor conductivity in long-term applications. Therefore, doping is required to improve and regulate its optoelectronic properties. Researchers have conducted extensive work on the doping modification of ZnO [5]-[10]. Among different doping elements, metallic Al and non-metallic F are the two most widely used dopants currently. Significant progress has been achieved in the optoelectronic properties of Al-doped ZnO (AZO) and F-doped ZnO (FZO) thin films, with their electrical conductivity and visible light transmittance reaching the order of 10^{-4} Ω·cm and 90%, respectively [11] [12]. Nevertheless, existing studies rarely analyze the effects of metallic Al and non-metallic F doping on the optoelectronic properties of ZnO systems from a microscopic perspective, especially by combining carrier transport mechanisms and optical response mechanisms.

In this study, first-principles calculation methods based on density functional theory (DFT) were used to calculate the structural properties, electronic structures, and optical properties of ZnO systems doped with metallic Al and non-metallic F. The influence mechanisms of metallic Al and non-metallic F on the optoelectronic properties of ZnO systems were explored.

2. Calculation Models and Methods

Figure 1 shows the conventional unit cell of ZnO, where red atoms represent oxygen (O) atoms and gray atoms represent zinc (Zn) atoms. The conventional unit cell of ZnO was expanded by 2 times along the x, y, and z directions respectively, resulting in a 2 × 2 × 2 supercell. This supercell contains 16 O atoms and 16 Zn atoms. Considering that substitutional doping is easier to carry out than interstitial doping, we used Al and F atoms to replace Z and O atoms respectively, with a doping concentration of 6.25 at.%.

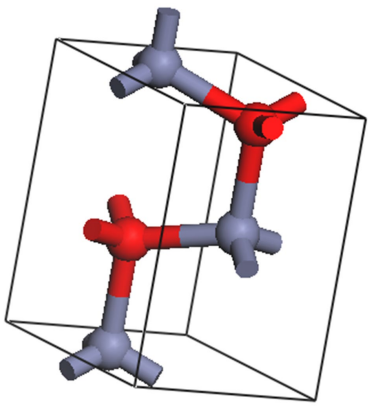

Figure 1. Conventional unit cell of ZnO. The red atoms represent O atoms, and the grey atoms represent Zn atoms.

The density functional calculation software package CASTEP was used to calculate the structural, electronic, and optical properties of pure ZnO and doped ZnO systems [13]. The exchange potential and correlation potential were described using the Perdew-Becke-Erzenhof functional within the generalized gradient approximation. The k-point grid and cutoff energy were set to $4 \times 4 \times 2$ and 360 eV, respectively. The convergence threshold for self-consistent iteration was set to 1×10^{-6} eV.

3. Results and Discussion

3.2. Structural Optimization

The optimized lattice parameters and differences in volume for the doped ZnO systems are listed in Table 1. The lattice parameters of pure ZnO are calculated as a = b = 3.293 Å, c = 5.304 Å, close to the experimental value [14]. After Al atom doping, the volume was reduced to 57.516 Å^3, with a volume change rate of 0.35%. In contrast, after F atom doping, the volume was increased to 58.699 Å^3, with a volume change rate of 2.06%. This phenomenon is mainly attributed to the differences in atomic radii between Al atom and Zn atom, as well as between F atom and Zn atom.

Table 1. Optimized lattice parameters and volume difference (ΔV) of doped ZnO systems.

Materials	Lattice parameters (Å)			V (Å^3)	ΔV (%)
	a	b	c		
Pure ZnO	3.293	3.293	5.304	57.516	/
Al-doped ZnO	3.288	3.288	5.304	57.314	−0.35
F-doped ZnO	3.313	3.313	5.348	58.699	2.06

3.2. Electronic Properties

Figure 2(a) shows the calculated band structure of pure ZnO. The red dotted line represents the Fermi energy level. It is found that the pure ZnO is a direct band gap semiconductor at the Z point. The calculated band gap value is 0.735 eV, which is consistent with the values reported in the literature [15] [16]. However, this value is much smaller than the experimental value, and this discrepancy is caused by the inherent limitations of the GGA functional itself, and does not affect the subsequent analysis of electronic structure and optical properties. Figure 2(b), Figure 2(c) show the band structures of doped ZnO. After Al and F atoms are doped into the ZnO lattice, the Fermi level enters the conduction band. The doped systems are transformed into n-type direct band gap semiconductors and exhibit metallic characteristics, with enhanced electrical conductivity. Electrons in the valence band are restricted by the Pauli exclusion principle and enter the conduction band above the Fermi level, leading to a widening of the optical band gap of the doped systems.

To further analyze the electronic structure, we calculated the total density of

states and partial density of states of pure ZnO and doped ZnO, as shown in Figure 3. In the electronic structure of pure ZnO, the density of states of Zn-3d orbitals is localized at deep energy levels. The valence band is mainly contributed by O-2p orbitals, while the conduction band is dominated by Zn- 4s and 4p orbitals. After Al is doped into ZnO, the 3s and 3p orbitals of Al introduce new impurity states near the Fermi level, which significantly increases the density of

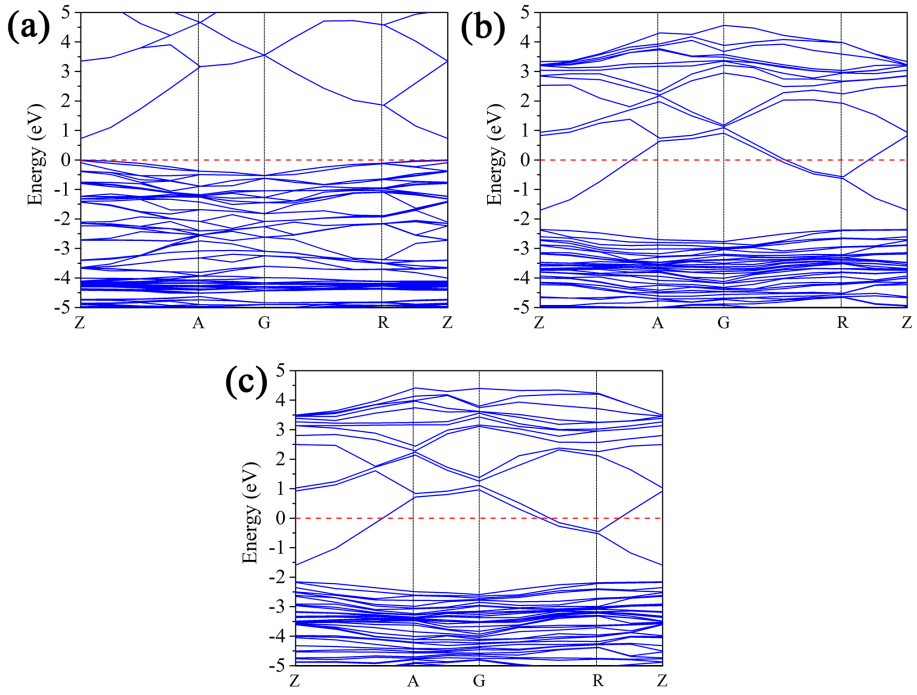

Figure 2. The band structures of (a) pure ZnO, (b) Al-doped ZnO, and (c) F-doped ZnO.

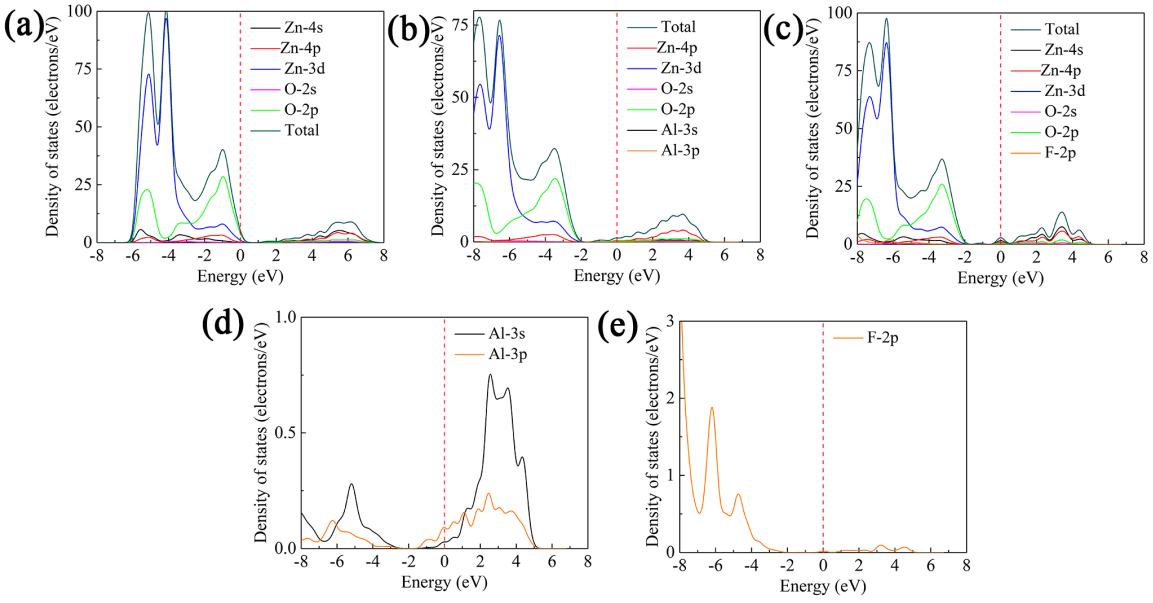

Figure 3. Density of states of (a) pure ZnO, (b) Al-doped ZnO, (c) F-doped ZnO, (d) Al atoms, and (e) F atoms.

states of the conduction band and is beneficial to the improvement of carrier concentration. For F-doped ZnO, the density of states of F-2p orbitals is distributed in the shallow energy level region and also makes contributions near the Fermi level, thus enhancing the electronic density of states of the conduction band. In conclusion, both Al and F doping introduce impurity states at the Fermi level in the electronic structure of ZnO, which helps to improve the carrier concentration and electrical conductivity of the doped systems.

In addition, to analyze the electron transport mechanism of different doped systems, the bending degree of the energy bands at the conduction band minimum (CBM) was compared. A larger curvature corresponds to a smaller effective mass, while a smaller curvature corresponds to a larger effective mass. Figure 4 presents the *E-K* diagrams along the horizontal direction and vertical direction. It can be observed from the figure that in the horizontal direction, the curvature of the CBM energy band of the F-doped ZnO system is larger than that of pure ZnO. In contrast, the curvature of the CBM energy band of the Al-doped ZnO system is smaller than that of pure ZnO. This indicates that the electron effective mass of the F-doped ZnO system in the horizontal direction is smaller than that of the Al-doped ZnO system. In the vertical direction, the curvatures of the CBM energy bands of both F-doped and Al-doped ZnO systems are smaller than that of pure ZnO, which means that the electron effective masses of the doped ZnO systems in the vertical direction are larger than that of pure ZnO. It is worth noting that the electron effective mass of the F-doped ZnO system in the vertical direction is smaller than that of the Al-doped ZnO system.

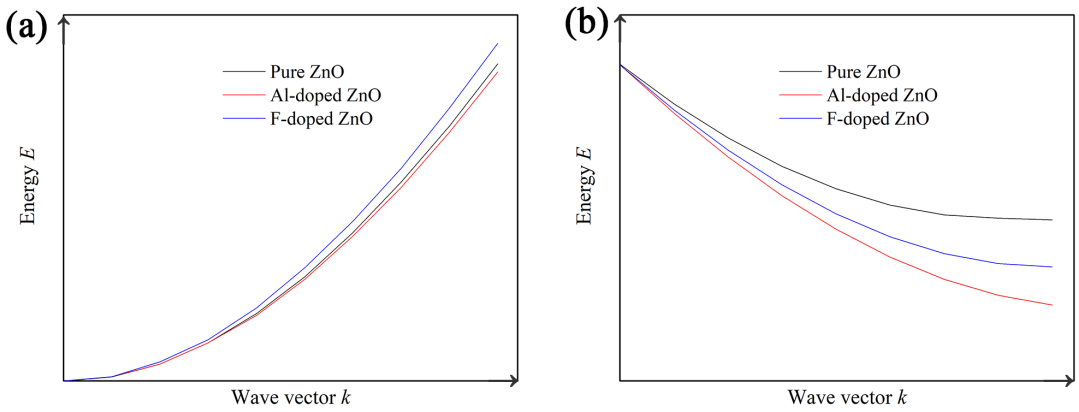

Figure 4. The *E-K* diagrams along the (a) horizontal and (b) vertical directions.

3.3. Optical Properties

The real and imaginary parts of the complex dielectric function can be obtained using the scissors operator method. With the values of these two parts, the absorbance and reflectance curves can be further calculated. Then, combined with the relationship of "Absorbance + Reflectance + Transmittance = 1", the transmittance spectra of pure ZnO, Al-doped ZnO, and F-doped ZnO were finally obtained, as shown in Figure 5. In the longer wavelength range of visible light, the

transmittance of the doped systems is slightly higher than that of pure ZnO, which is caused by the lower reflectance. In the shorter wavelength range of visible light and the larger wavelength range of ultraviolet light, the transmittance of the doped systems is significantly higher than that of pure ZnO, which is mainly attributed to the increase in optical band gap. From the perspective of electronic structure, electrons in the O-2p orbitals of the valence band absorb photon energy and then jump to the Al-3p, F-2p, and Zn-4p orbitals above the Fermi level, resulting in a blue shift of the absorption edge. In the visible light band, the Al-doped ZnO system and the F-doped ZnO system exhibit similar transmittance properties, with both transmittances reaching more than 90%, which is consistent with the results reported in previous experiments [11] [12].

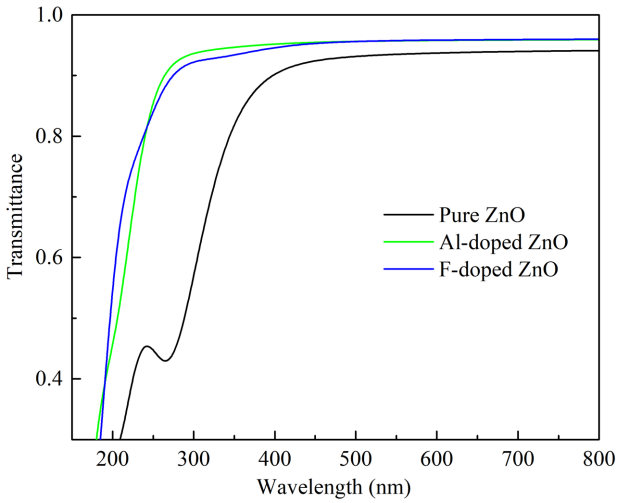

Figure 5. Transmittance of pure ZnO and doped systems.

4. Conclusion

In this paper, the structure, electronic and optical properties of the Al- and F-doped ZnO have been investigated by the first-principles study based on the density functional theory. The calculated lattice constants of ZnO are in agreement with experimental values. The incorporation of F and Al elements modifies the electronic structure of ZnO, transforming ZnO into an n-type semiconductor with an increased optical band gap and enhanced electrical conductivity. The electron effective masses of F-doped ZnO in both horizontal and vertical directions are smaller than those of Al-doped ZnO, indicating that F-doped ZnO exhibits higher electron mobility. The calculation results of optical properties show that the incorporation of F and Al elements increases the transmittance of ZnO in the short-wavelength range of visible light and the long-wavelength range of ultraviolet light, and both doped systems exhibit similar transmittance characteristics in the visible light band, with both transmittances reaching more than 90%.

Acknowledgements

This work was supported by Yunnan Provincial Department of Education Scien-

tific Research Fund Project (2025J2031) and Yunnan Open University University-Level Research Fund Project (2025G12, 24YNOU54).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Chavan, G.T., Kim, Y., Khokhar, M.Q., Hussain, S.Q., Cho, E., Yi, J., *et al.* (2023) A Brief Review of Transparent Conducting Oxides (TCO): The Influence of Different Deposition Techniques on the Efficiency of Solar Cells. *Nanomaterials*, **13**, Article 1226. https://doi.org/10.3390/nano13071226

[2] Ramanathan, G. and Murali, K.R. (2022) Optical Performance of Tin Doped Indium Oxide (ITO) Thin Films Prepared by Sol Gel Dip Coating Techniques Using Acrylamide Route. *Optical and Quantum Electronics*, **54**, Article 652. https://doi.org/10.1007/s11082-022-03973-5

[3] Yang, J., Jiang, Y., Li, L. and Gao, M. (2017) Structural, Morphological, Optical and Electrical Properties of Ga-Doped ZnO Transparent Conducting Thin Films. *Applied Surface Science*, **421**, 446-452. https://doi.org/10.1016/j.apsusc.2016.10.079

[4] Agura, H., Suzuki, A., Matsushita, T., Aoki, T. and Okuda, M. (2003) Low Resistivity Transparent Conducting Al-Doped ZnO Films Prepared by Pulsed Laser Deposition. *Thin Solid Films*, **445**, 263-267. https://doi.org/10.1016/s0040-6090(03)01158-1

[5] Khuili, M., Fazouan, N., El Makarim, H.A., Atmani, E.H., Rai, D.P. and Houmad, M. (2020) First-Principles Calculations of Rare Earth (RE=Tm, Yb, Ce) Doped ZnO: Structural, Optoelectronic, Magnetic, and Electrical Properties. *Vacuum*, **181**, Article ID: 109603. https://doi.org/10.1016/j.vacuum.2020.109603

[6] Matur, U.C., Duru, I.P. and Akcan, D. (2022) Tracking Optical Properties of ZnO:Mg Thin Films: Experimental and First Principles Calculations. *Ceramics International*, **48**, 19090-19097. https://doi.org/10.1016/j.ceramint.2022.03.199

[7] Li, Z., Li, J., Lei, J., Xiong, M., Wang, N. and Zhang, S. (2021) First-Principles Study of Structure, Electrical and Optical Properties of Al and Mo Co-Doped ZnO. *Vacuum*, **186**, Article ID: 110062. https://doi.org/10.1016/j.vacuum.2021.110062

[8] Akhond, M.R. and Sharif, A. (2020) Role of Hydrogen Co-Doping on Opto-Electronic Behaviors of Na-H Co-Doped Zinc Oxide: A First Principle Study. *Journal of Physics Communications*, **4**, Article ID: 115002. https://doi.org/10.1088/2399-6528/abc672

[9] Qing, X., Zhang, C., Gong, J. and Chen, S. (2021) *Ab Initio* Study of Photoelectric Properties in ZnO Transparent Conductive Oxide. *Vacuum*, **191**, Article ID: 110391. https://doi.org/10.1016/j.vacuum.2021.110391

[10] Ma, J., Zhang, W., Lin, J., Sun, Y., Ma, J., Xu, H., *et al.* (2020) Theoretical Study on Group III Elements and F Co-Doped ZnO. *Journal of Alloys and Compounds*, **819**, Article ID: 153012. https://doi.org/10.1016/j.jallcom.2019.153012

[11] Zhang, D., Yu, W., Zhang, L. and Hao, X. (2023) Progress in the Synthesis and Application of Transparent Conducting Film of AZO (ZnO:Al). *Materials*, **16**, Article 5537. https://doi.org/10.3390/ma16165537

[12] Wang, F., Chen, M., Liu, H. and Kang, T. (2022) Effect of Rapid Thermal Annealing Time on ZnO:F Thin Films Deposited by Radio Frequency Magnetron Sputtering for Solar Cell Applications. *Applied Physics A*, **128**, Article No. 227.

https://doi.org/10.1007/s00339-022-05376-5

[13] Segall, M.D., Lindan, P.J.D., Probert, M.J., Pickard, C.J., Hasnip, P.J., Clark, S.J., *et al.* (2002) First-Principles Simulation: Ideas, Illustrations and the CASTEP Code. *Journal of Physics*: *Condensed Matter*, **14**, 2717-2744. https://doi.org/10.1088/0953-8984/14/11/301

[14] Kisi, E.H. and Elcombe, M.M. (1989) U Parameters for the Wurtzite Structure of ZnS and ZnO Using Powder Neutron Diffraction. *Acta Crystallographica Section C Crystal Structure Communications*, **45**, 1867-1870. https://doi.org/10.1107/s0108270189004269

[15] Zhang, M., Zhang, C. and Shen, J. (2011) First-Principles Calculation of Electronic Structure of $Mg_xZn_{1-x}O$ Codoped with Aluminium and Nitrogen. *Chinese Physics B*, **20**, 017101. https://doi.org/10.1088/1674-1056/20/1/017101

[16] Yang, P., Zhao, Y. and Yang, H. (2015) Investigation on Optoelectronic Performances of Al, N Codoped ZnO: First-Principles Method. *Ceramics International*, **41**, 2446-2452. https://doi.org/10.1016/j.ceramint.2014.10.059