Journal of Materials Science and Chemical Engineering, 2025, 13(12), 78-85
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/F Co-Doped ZnO

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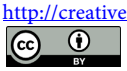
How to cite this paper: Xiao, X.J., Wang, J.F., Li, D.C., Kang, K.Y. and Zhu, H.M. (2025) First-Principles Study on the Electronic and Optical Properties of Al/F Co-Doped ZnO. *Journal of Materials Science and Chemical Engineering*, **13**, 78-85.
https://doi.org/10.4236/msce.2025.1312004

Received: November 6, 2025
Accepted: December 15, 2025
Published: December 18, 2025



Abstract

Based on density functional theory (DFT), this study used first-principles calculations to explore the electronic and optical properties of Al/F co-doped ZnO. The results show that the Al-3s, Al-3p, and F-2p orbitals introduce impurity states near the Fermi level, thereby enhancing the electrical conductivity of the co-doped system. Al/F co-doped ZnO is an n-type direct semiconductor with the average transmittance of 93.9% in the wavelength range of 400 nm to 1400 nm. This study provides theoretical guidance for the preparation of Al and F co-doped ZnO thin films.

Keywords

DFT, Al/F Co-Doped ZnO, Electronic Structure, Optical Property

1. Introduction

As a typical wide-bandgap semiconductor material, ZnO demonstrates promising applications in transparent conductive films, ultraviolet detectors, and solar cell window layers due to its excellent optoelectronic properties, chemical stability, and low-cost advantages [1]-[3]. However, the intrinsic carrier concentration, electrical and optical transparency of pure ZnO are difficult to meet the practical needs of high-performance devices. Therefore, doping modification can be used to regulate its optoelectronic properties. Compared to single doping, co-doping strategy can achieve precise control of the electronic structure and optical properties of ZnO through the synergistic effect between different elements. When III and VII elements are co-doped, the synergistic substitution of cations and anions can increase the carrier concentration and suppress lattice distortion, thereby enhancing the conductivity and stability of the material. Starowicz *et al.* [4] success-

fully prepared Al/F co-doped ZnO thin films (FAZO) with high transparency and band gap energies of 3.53 - 3.58 eV by atomic layer deposition. Wang *et al.* [5] fabricated FAZO films via radio-frequency magnetron sputtering, and the films exhibited a mobility of 53.97 cm^2/Vs, a resistivity of 2.23×10^{-4} Ω cm, a carrier concentration of 5.18×10^{20} cm^{-3}, and an average transmittance over 90% in the range of 400 - 1200 nm. The same method was used to study the effect of substrate temperature on the FAZO films [6]. The results show that when the substrate temperature is 440˚C, the films exhibit good performance. However, the synergistic mechanism of Al and F atoms remains unclear and requires further exploration.

In our previous work, we have calculated the structural, electronic, and optical properties of Al-doped ZnO or F-doped ZnO using first-principles methods [7]. In this paper, we adopt the same approach to investigate the effect of Al and F co-doping on the optoelectronic properties of ZnO, aiming to provide useful guidance for the future preparation of Al and F co-doped ZnO thin films.

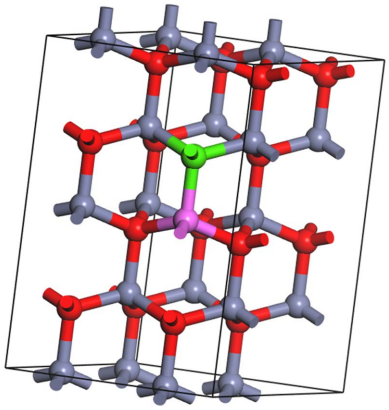


Figure 1. Crystal structure of Al/F co-doped ZnO. The red atoms represent O atoms, and the grey atoms represent Zn atoms. The pink and green colors represent the Al and F atoms, respectively.

2. Calculation Models and Methods

Considering that the stability of adjacent co-doping structures of metals and non-metals is higher than that of other doping structures, the ZnO structure with adjacent co-doping of Al and F atoms was selected as the research object in this study [8] [9]. **Figure 1** shows the 2 × 2 × 2 supercell structure diagram of Al/F co-doped ZnO. In the supercell model, a Zn atom is replaced by an Al atom, and one of its adjacent O atoms is replaced by an F atom. We calculated the photoelectric properties of Al/F co-doped ZnO system by using he density functional calculation software package CASTEP for this study [10]. The valence electron configuration of Zn, O, Al, and F was $3s^2 3p^6 3d^{10} 4s^2$, $2s^2 2p^4$, $3s^2 3p^1$, and $2s^2 2p^5$, respectively. The generalized gradient approximation Perdew-Becke-Erzenhof function was used to describe the exchange and correlation potentials. All basic parameter settings were the same as our previous work [7]. The settings for energy cutoff, k-point mesh, and convergence criteria are 4 × 4 × 2, 360 eV, and 1×10^{-6} eV, respectively.

3. Results and Discussion

3.1. Electronic Properties

Figure 2 shows the calculated results of the band structure and density of states (DOS) of Al/F co-doped ZnO. In the band structure of the co-doped ZnO system, the Fermi level crosses the conduction band, exhibiting n-type electrical conductivity. The conduction band minimum and valence band maximum correspond to the same Z point in the Brillouin zone, indicating that the Al/F co-doped ZnO system is a direct semiconductor. The total density of states shows that the low-energy region is dominated by the Zn-3d orbitals, the mid-energy region is contributed to by the O-2p and Zn-4p orbitals, and the high-energy region (near the Fermi level) involves the Zn-4s, Zn-3d, Al-3p, and F-2p orbitals, indicating a large number of carriers in the conduction band. In the partial density of states of Al atoms, the Al-3p orbitals make significant contributions near and above the Fermi level, providing a large number of free electrons for the system. The partial density of states of F atoms shows that the F-2p orbitals mainly participate in bonding in the low and mid-energy regions, indirectly assisting Al in enhancing the carrier concentration. Figure 3 displays the total density of states of different doped systems. The carrier occupation probability in the doped ZnO systems can be intuitively observed from the area enclosed by the total density of states from the valence band maximum to the Fermi level and the horizontal axis. Compared with the single-doped ZnO system, the Al/F co-doped ZnO system has a larger area, implying that the co-doping of Al and F atoms leads to a higher carrier concentration in the Al/F co-doped ZnO system.

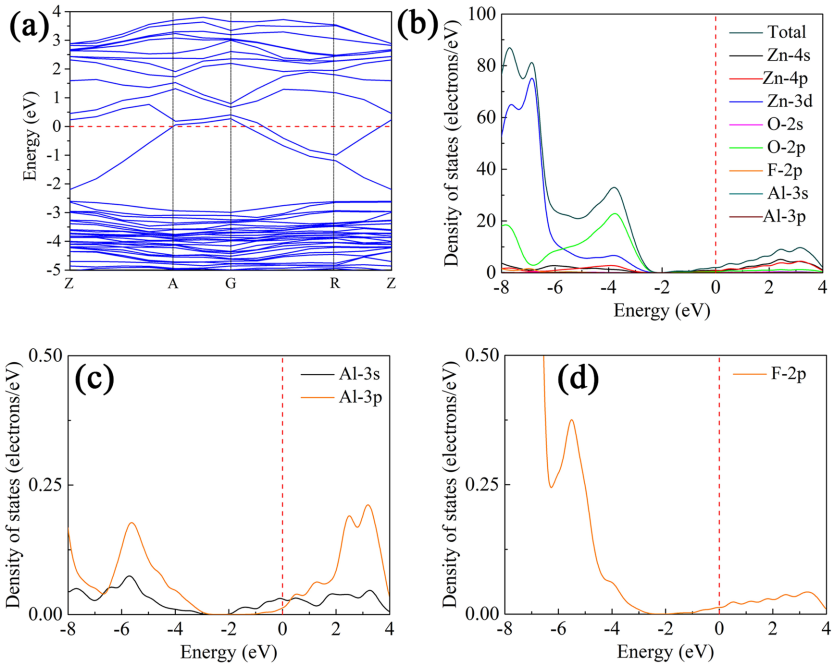


Figure 2. (a) Band structures and (b) density of states of Al/F co-doped ZnO, (c) density of states of (c) Al atoms, and (d) F atoms.

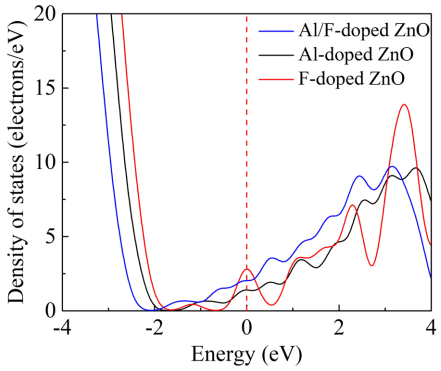


Figure 3. Total density of states of doped ZnO systems.

To further investigate the electron transport properties of the Al/F co-doped ZnO system, we compared the bending degrees of the conduction band minimum (CBM) and valence band maximum (VBM) curves, as shown in **Figure 4**. The Al/F co-doped ZnO system exhibits a larger curvature in the horizontal direction than the single-doped systems, corresponding to a smaller electron effective mass. In contrast, its curvature in the vertical direction is smaller than that of the single-doped systems, resulting in a larger electron effective mass. Here, m_a^* and m_b^* represent the effective masses in the horizontal and vertical directions, respectively. For the convenience of comparison, m denotes the average effective mass across different directions. The values of m_a^*, m_b^*, and m were calculated using Equations (1) and (2), and the results are presented in **Table 1**.

$$\frac{1}{m^*} = \frac{1}{h^2}\frac{d^2E(k)}{dk^2} \tag{1}$$

$$\frac{3}{m} = \frac{2}{m_a^*} + \frac{1}{m_b^*} \tag{2}$$

As can be seen from **Table 1**, the electron effective mass of the Al/F co-doped ZnO system in the horizontal direction is smaller than that of the single-doped systems, while its electron effective mass in the vertical direction is larger. Notably, the average effective mass of the Al/F co-doped ZnO system is 0.126 m_0, which is comparable to that of the single-doped systems.

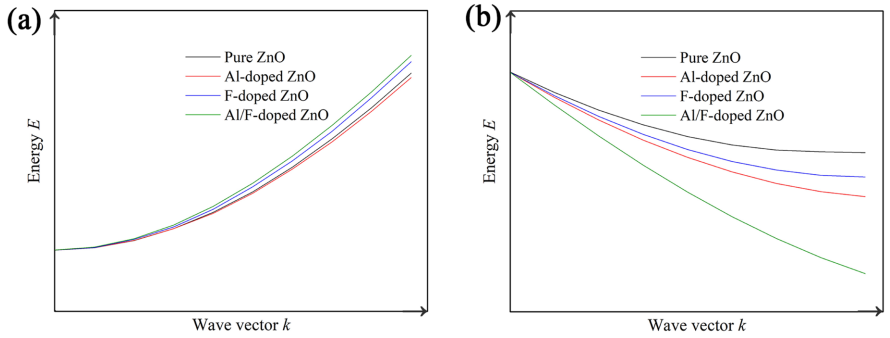


Figure 4. The *E-K* diagrams along the (a) horizontal and (b) vertical directions for different doped ZnO systems.

Table 1. The effective mass of the different doped ZnO systems.

Materials	m_a^* (m_0)	m_b^* (m_0)	m^* (m_0)
Al-doped ZnO	0.125	0.141	0.129
F-doped ZnO	0.141	0.130	0.119
Al/F co-doped ZnO	0.112	0.172	0.126

3.2. Mulliken Analysis

The Mulliken population is a crucial quantitative parameter for characterizing the electron distribution features of atoms and chemical bonds. Through precise calculation and analysis, the bonding nature, charge distribution characteristics, and charge transfer pathways of ZnO can be revealed. Table 2 presents the Mulliken populations of the undoped ZnO and doped ZnO systems. The Mulliken population of the Zn-O bond in undoped ZnO is 0.41, indicating that the Zn-O bond in undoped ZnO is inclined to be ionic. After Al and F atoms enter the ZnO lattice, the population of the Zn-O bond decreases, leading to an enhancement in its ionic character. It is noteworthy that the population of the Al-O bond increases, resulting in an enhancement of its covalent character, while the population of the Al-F bond decreases, leading to an enhancement of its ionic character. The population of the Zn-F bond is 0.035, which is quite small. This implies that the electron cloud overlap between Zn and F atoms is very low, and this chemical bond is dominated by ionic character with very weak covalent character. From the calculation results of the average Mulliken charge of atoms, in undoped ZnO, one Zn atom donates 0.83 electrons, and one O atom accepts 0.83 electrons. The charge distribution changes due to the doping of Al and F atoms. The Mulliken charge of the Al atom is close to twice that of the Zn atom, which means that the Al atom provides more electrons to the doped system. In addition, the Mulliken charge of the O atom decreases from −0.82 to −0.57, indicating that the number of electrons it gains decreases, thus providing more electrons to the system. Therefore, the incorporation of Al and F atoms contributes more electrons to the ZnO system, enhancing its electrical conductivity, which is consistent with the analysis results of the band structure and density of states.

Table 2. Mulliken populations of pure ZnO and doped system.

System	Mulliken population of bands				Mulliken charge of atoms (|e|)			
	Zn-O	Al-O	Al-F	Zn-F	Zn	O	Al	F
Pure ZnO	0.41	/	/	/	0.82	−0.82	/	/
Doped system	0.361	0.520	0.300	0.035	0.758	−0.823	1.52	−0.57

3.3. Optical Properties

Figure 5 shows the absorption, reflectivity, and transmittance curves of the Al/F co-doped ZnO system. From the optical absorption curve (Figure 5(a)), the Al/F

co-doped ZnO exhibits strong absorption capacity in the ultraviolet (UV) region, with a maximum absorption coefficient of 1.39×10^5 cm^{-1}. Compared with pure ZnO, both the position and intensity of the absorption peak have changed significantly. This indicates that the co-doping of Al and F introduces new impurity energy levels, which alters the mode of electron transition. The peak appearing in the visible light region is attributed to the electron transition from the O-2p orbital in the valence band to the Al-3p/Al-3s/F-2p orbitals. For the reflectivity (**Figure 5(b)**), the reflectivity of Al/F co-doped ZnO is significantly lower than that of pure ZnO across the entire wavelength range, especially in the UV region. This implies that the introduction of Al and F atoms reduces the reflectivity of the ZnO system. The transmittance of Al/F co-doped ZnO was calculated from its absorption and reflection data, as shown in **Figure 5(c)**. The transmittance of Al/F co-doped ZnO above 500 nm is higher than that of pure ZnO, which is caused by its lower reflectivity. Compared with Al or F-doped ZnO, the Al/F co-doped ZnO shows a similar transmittance curve above 600 nm, but its transmittance near 350 nm is poorer. This phenomenon is related to the change in the electron transition mechanism of impurity states. The average transmittance of the Al/F co-doped ZnO system in the 400 - 1400 nm wavelength range is 93.9%, exceeding 90%, which is consistent with the experimental results [5] [6].

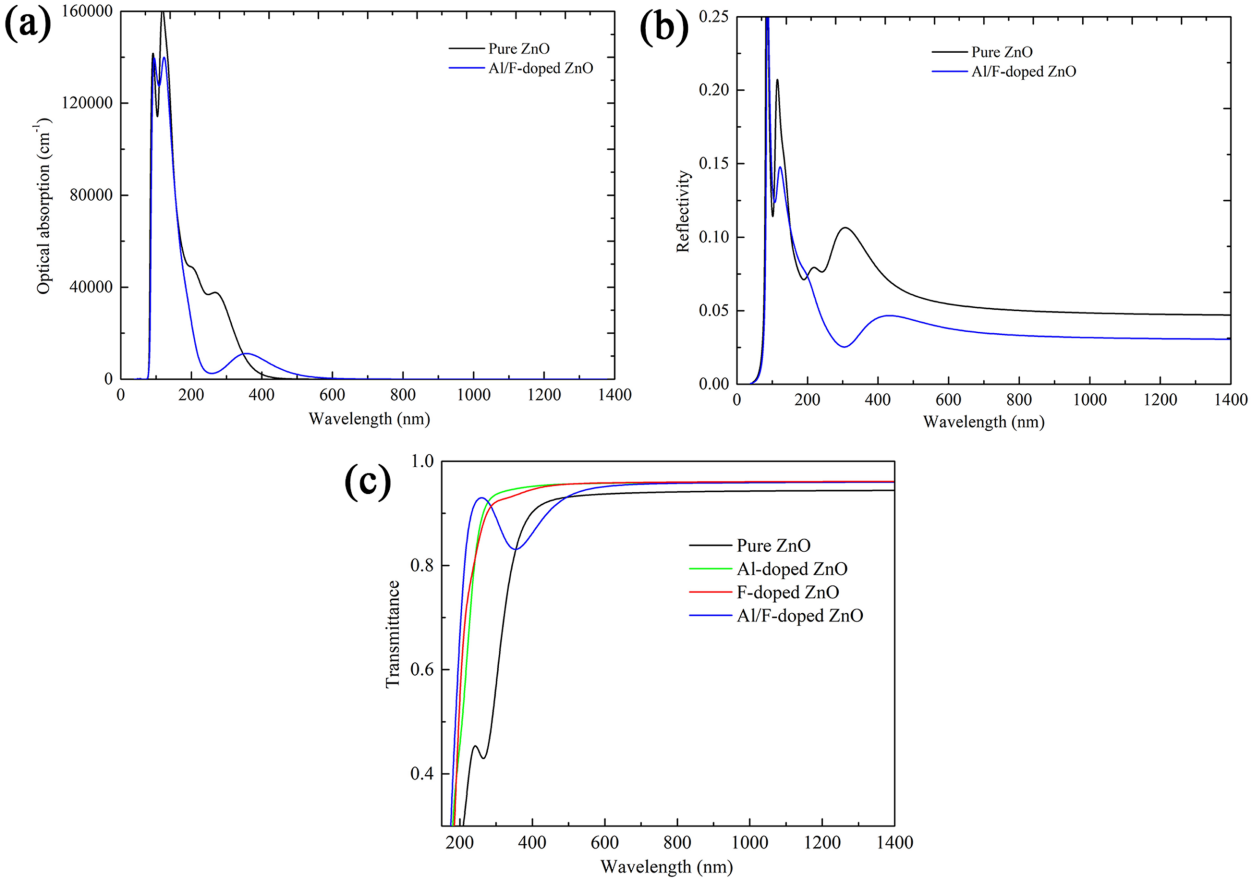


Figure 5. (a) Absorption, (b) reflectivity, and (c) transmittance of Al/F co-doped ZnO.

4. Conclusions

This paper explores the effect of Al and F co-doping on the electronic and optical properties of ZnO using first-principles calculations. Al/F co-doping introduces impurity states near the Fermi level, endowing the co-doped system with n-type semiconductor characteristics and increasing the carrier concentration. Mulliken analysis reveals that Al and F atoms provide additional free electrons for the co-doped system. Al/F co-doped ZnO has smaller horizontal electron effective mass (0.112 m_0) and larger vertical one (0.172 m_0) than single-doped systems, with average effective mass (0.126 m_0) comparable to them. Optically, it has strong UV absorption and 93.9% average transmittance in 400 - 1400 nm.

In summary, Al/F co-doped ZnO possesses both high carrier concentration, excellent electron transport properties, and a high average transmittance of 93.9% in the 400 - 1400 nm wavelength range, showing great potential as a window layer in solar cells or a transparent conductive electrode in high-efficiency optoelectronic devices. Our calculation results provide important theoretical support for the practical development and application of this material in the field of transparent conductive oxides.

Acknowledgements

This work was supported by Yunnan Provincial Department of Education Scientific 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.

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