

Article

Investigation of Electronic and Optical Properties of Al/Ag and Al/N Co-Implanted ZnO Thin Films

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Abstract: Either metal/metal or metal/non-metal co-doping is one of the most effective methods to modulate the visible emission of ZnO. In this paper, ZnO, aluminum-doped ZnO (Al-ZnO), aluminum and silver co-doped ZnO (Al/Ag-ZnO), and aluminum and nitrogen co-doped ZnO (Al/N-ZnO) are deposited. Combining the substitution of zinc ions using Al and/or Ag doping and the substitution of oxygen ions using N doping is expected to introduce more interstitial zinc and oxygen vacancy defects related to visible light emission in ZnO films. The results indicate that the PL spectrum of ZnO shows a violet emission peak at 406 nm and other weak visible emission peaks. After Al doping, we observe a strong blue emission at 421 nm, and its intensity is further enhanced and attains the maximum for Al/N-ZnO. However, for Al/Ag-ZnO, the blue emission shifts toward a longer wavelength, and the intensity of the blue emission conversely decreases. Then, the band structures, the density of states (DOS), the partial density of states (PDOS), and the optical constant of doped ZnO are calculated using density functional theory (DFT). Based on the experimental and theoretical results, the enhancement mechanism of visible light is discussed.

Keywords: ZnO; band structures; XRD; electronic properties; luminescence properties



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1. Introduction

ZnO materials have attracted increasing interest because of their wide bandgap (~3.37 eV) and large exciton binding energy (~60 meV) [1,2]. Based on these two excellent properties, it is utilized as a candidate material for photoelectric devices and has some potential applications, such as transparent electrodes, ultraviolet lasers, light emission diodes, and solar cells [3–7]. As one of the most important performances, its optical properties have attracted increasing attention. Alnoor et al. [8] concluded that the ZnO seed layer plays a key role in the defect density at the ZnO-based heterostructure interface. Nosidlak et al. [9] reported the thermal–optical coefficient of Al-doped ZnO, including optical properties. Tabib et al. [10] discussed the optical properties of sodium-doped ZnO nanocrystals and explored their potential application in solar photocatalysis. Rao et al. [11] integrated node-like ZnO, sheet-like ZnO, and rod-like ZnO into white light-emitting diodes to improve the uniformity of angular correlated color temperature (CCT). Kuang et al. [12] found that the performance of UV photodetectors based on ZnO arrays was improved under the modification of polyethyleneimine.

The photoluminescence (PL) spectrum of ZnO contains two characteristic emission bands. One is a sharp ultraviolet emission; the other is located in the visible region, which is relatively broader and weaker than the ultraviolet peak [13]. Although a large number of previous studies focus on the enhancement and potential application of ultraviolet emission [14,15], the investigation of the visible emission of ZnO is necessary due to its potential applications in white light-emitting diodes. Li et al. [16] fabricated white light-emitting diodes based on the visible emission of p-type ZnO nano-arrays with high-level

Fe impurities. Ikhioya et al. [17] reported the improved optical properties of ZnO by introducing the erbium (Er) dopant. Meng et al. [18] achieved bright green luminescence from ZnO films prepared by the reaction of oxygen and zinc powder. Zeng et al. [19] introduced high-concentration defects by non-equilibrium processes to improve blue emission.

Generally, the luminescence of ZnO in the visible region is related to the defect concentration [5], which can be regulated by various methods, among which doping is one of the most effective. However, the quenching of light emission occurs if too many defects are introduced. Solving this contradiction is the key issue to improve the visible light emission in ZnO. In this paper, ZnO, combining the substitution of zinc ions using Al and/or Ag doping and the substitution of oxygen ions using N doping is expected to introduce more interstitial zinc and oxygen vacancy defects related to visible light emission in ZnO films. Firstly, various doped ZnO are deposited, including metal single doping ZnO (Al-ZnO), metal/metal co-doping ZnO (Al/Ag-ZnO), and metal/non-metal co-doping ZnO (Al/N-ZnO). Then, the crystal structure, band structures, density of states (DOS), partial density of states (PDOS), optical constant, and PL properties of various doped ZnO are investigated based on experimental characterization and theoretical calculation. Finally, the enhancement mechanism of visible emission is discussed.

2. Experimental Details and Computational Methods

2.1. Experimental Details

Before sample preparation, the glass substrates are ultrasonically cleaned for 15 min, and washed in sequence with acetone and ethanol. Next, they are soaked, cleaned, and dried with 5% hydrofluoric acid solution, distilled water, and nitrogen, respectively. Then, the cleaned substrates are placed into the sputtering chamber, and clamped on a sample tray 50 mm away from the high-purity ZnO target (99.99%, 60 mm in diameter). The type of device used is JCPY-500 (Technol, Beijing, China). Finally, the vacuum chamber is pumped to 4.5×10^{-5} Pa. Ar gas is introduced and the reaction pressure is maintained at 1.2 Pa. The ZnO target is pre-sputtered for 10 min. A substrate temperature of room temperature, a sputtering power of 200 W, an argon gas flow of 35 sccm, and a sputtering time of 1 h are used. Al content is maintained at 3 at.% to obtain Al-ZnO. At the same time, the concentrations of Al and Ag are maintained at 3 at.% to prepare Al/Ag-ZnO. In addition, nitrogen gas of 35 sccm is introduced during the magnetron sputtering to achieve Al/N-ZnO. Finally, the samples are annealed at 350 °C in a vacuum to obtain a high percentage of interstitial zinc.

2.2. Computational Methods

Using the Materials Studio software (version 8.0, Accelrys, China) with Cambridge Serial Total Energy Package (CASTEP) module, based on the first principle, all calculations are performed using density functional theory (DFT) [20]. The electronic exchange correlation is disposed of by generalized gradient approximation (GGA), which belongs to the Perdew–Burke–Ernzerhof (PBE) functional [21]. The K point and the cutoff energy are set to $8 \times 8 \times 1$ and 450 eV, respectively. The optimized structure of ZnO (a), metal single doping ZnO (Al-ZnO) (b), metal/metal co-doping ZnO (Al/Ag-ZnO) (c), and metal/non-metal co-doping ZnO (Al/N-ZnO) (d) is shown in Figure 1. The $2 \times 2 \times 2$ supercell consisting of 32 atoms is constructed. Zn atom is replaced by a metal impurity (Al or/and Ag) atom, and O atom is replaced by a non-metallic impurity (N) atom to construct doped ZnO. A Brillouin zone path (G→A→H→K→G→M→L→H) is set to calculate the energy band structure.

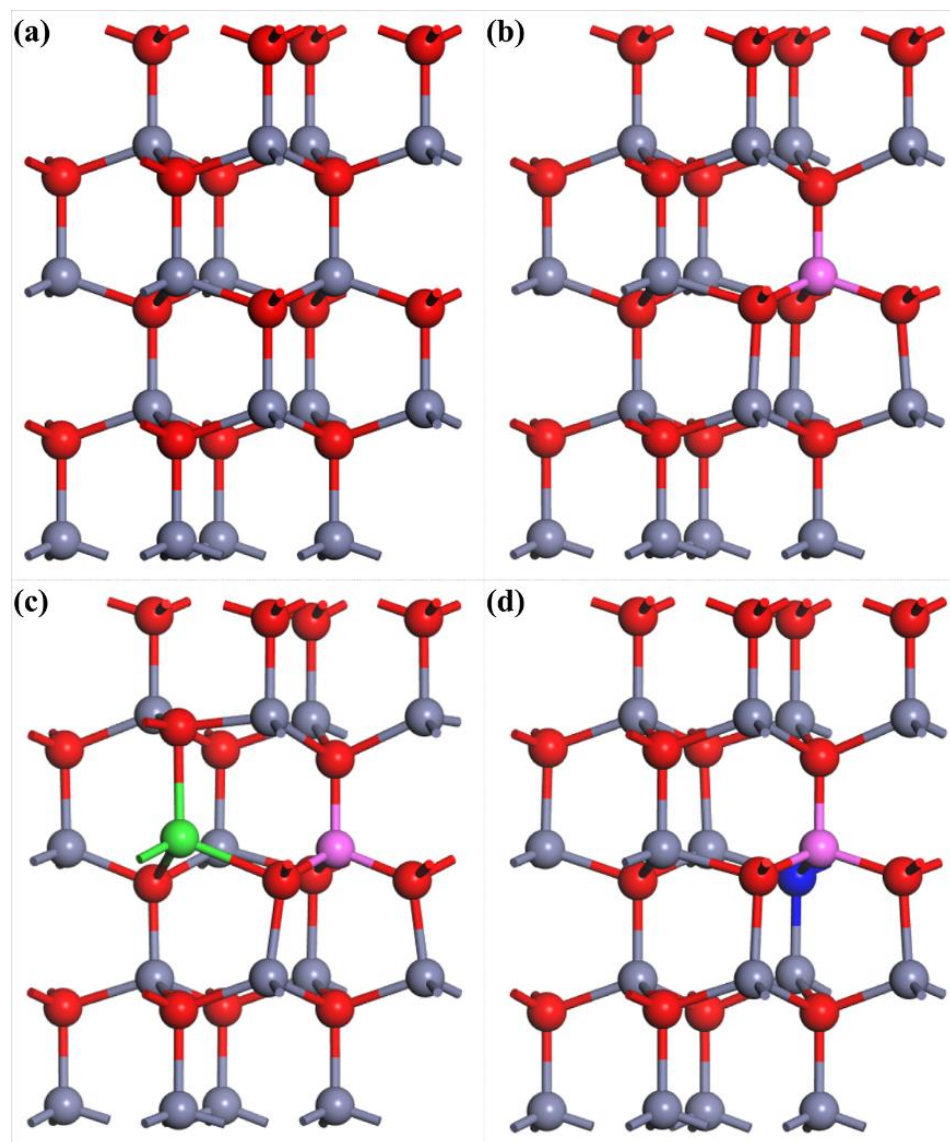


Figure 1. Optimized $2 \times 2 \times 2$ supercell of ZnO (a), metal single doping ZnO (Al-ZnO) (b), metal/metal co-doping ZnO (Al/Ag-ZnO) (c), and metal/non-metal co-doping ZnO (Al/N-ZnO) (d), and the red, gray, pink, green, and blue spheres represent oxygen, zinc, aluminum, silver, and nitrogen atoms, respectively.

3. Results and Discussion

Figure 2 shows the XRD patterns of ZnO (a), metal single doping ZnO (Al-ZnO) (b), metal/metal co-doping ZnO (Al/Ag-ZnO) (c), and metal/non-metal co-doping ZnO (Al/N-ZnO) (d). All of the samples show good crystallinity, and the (002) diffraction peaks of Al/Ag ZnO and Al/N-ZnO are significantly enhanced, indicating that the samples have a preferred orientation of the c axis perpendicular to substrates. The 2θ values are 34.39° , 34.13° , 34.48° , and 34.32° , corresponding to ZnO, Al-ZnO, Al/Ag-ZnO, and Al/N-ZnO, respectively. Meanwhile, different doping leads to the change of the (002) peak intensity, which reaches the maximum for Al and N co-doped ZnO. In addition, different doping also changes the full width at half maxima (FWHM) of the ZnO (002) diffraction peak, whose minimum value is about 0.24° . Interestingly, it is observed for Al and Ag co-doped ZnO. In addition, comparing the diffraction parameters of all samples, the maximum change rate of FWHM is 61.5% ($0.24/0.39$).

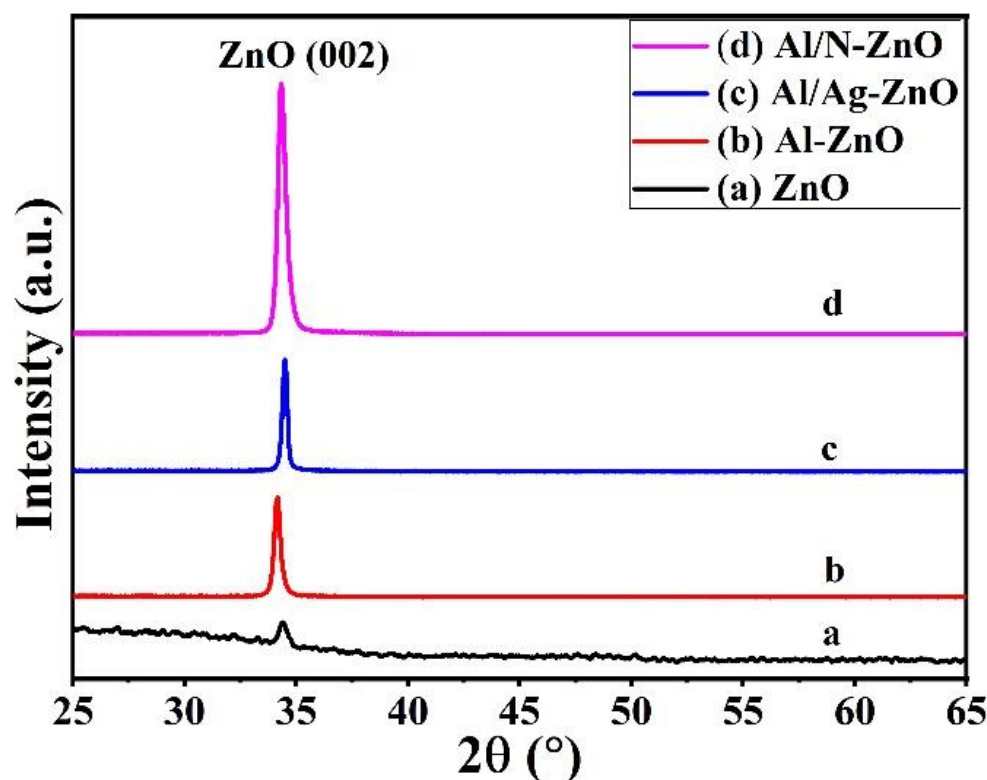


Figure 2. XRD patterns of ZnO (a), metal single doping ZnO (Al-ZnO) (b), metal/metal co-doping ZnO (Al/Ag-ZnO) (c), and metal/non-metal co-doping ZnO (Al/N-ZnO) (d).

Based on the Scherrer formula [22], the average grain size D is calculated:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where the symbols λ , β , and θ denote the X-ray wavelength (1.5406 Å), FWHM, and diffraction angle of the ZnO (002) peak, respectively.

In order to analyze the effect of doping on the electrical and optical properties of ZnO from the aspect of electronic structure, and to compare with the experimental results, the energy bands and density of states (DOS) of the structure are calculated by DFT. In Figure 3, there are band structures of ZnO (a), metal single doping ZnO (Al-ZnO) (b), metal/metal co-doping ZnO (Al/Ag-ZnO) (c), and metal/non-metal co-doping ZnO (Al/N-ZnO) (d). The results show that the bandgap of ZnO is 0.745 eV, and it is still a direct bandgap semiconductor. Since both the conduction band minimum (CBM) and valence band maximum (VBM) are at the G point, the band types of ZnO do not change after doping. Compared with pristine ZnO, Al-doped, Al/Ag co-doped, and Al/N co-doped ZnO decrease the bandgap, and the corresponding values are 0.673, 0.213, and 0.574 eV, respectively. The Fermi level of Al-ZnO moves upward and enters the conduction band, so the electron concentration in the valence band increases, which meets the conditions for forming n-type semiconductors. However, when Ag or N atoms enter into Al-ZnO, the Fermi level moves down and enters the valence band; thus, the conduction type is changed to p-type.

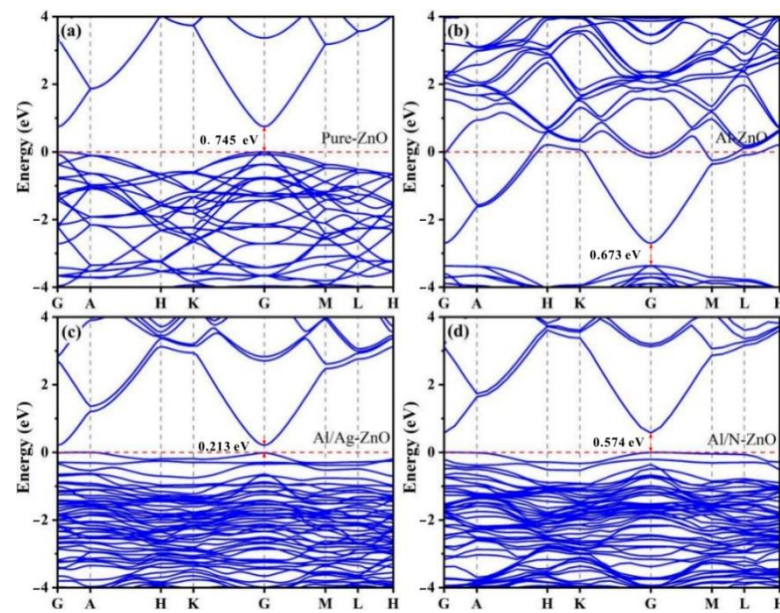


Figure 3. Band structures and band gaps of ZnO (a), metal single doping ZnO (Al-ZnO) (b), metal/metal co-doping ZnO (Al/Ag-ZnO) (c), and metal/non-metal co-doping ZnO (Al/N-ZnO) (d), respectively. The Fermi level is set to zero.

According to the Tauc relationships [23], the direct bandgap of samples is calculated:

$$\alpha h\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (2)$$

where the symbols α , h , ν , A , and E_g are the absorption coefficient, Planck's constant, the photon frequency, a constant, and the optical bandgap, respectively. Figure 4 illustrates $(\alpha h\nu)^2$ vs. $h\nu$ plots of ZnO (a), metal single doping ZnO (Al-ZnO) (b), metal/metal co-doping ZnO (Al/Ag-ZnO) (c), and metal/non-metal co-doping ZnO (Al/N-ZnO) (d). In the region with high photon energy, if $(\alpha h\nu)^2$ and $h\nu$ have a linear relationship, it indicates that the sample is a direct bandgap semiconductor. According to the position where the linear fitting line intersects the horizontal axis ($\alpha h\nu = 0$), the optical bandgap E_g value can be obtained. The E_g values of ZnO is 3.98 eV; however, it is decreased to 3.59 eV, 3.80 eV, and 3.44 eV for metal single doping ZnO (Al-ZnO), metal/metal co-doping ZnO (Al/Ag-ZnO), and metal/non-metal co-doping ZnO (Al/N-ZnO), respectively.

To further systematically understand the electronic structure, both the DOS and PDOS are calculated, as shown in Figure 5. For ZnO, there are two strong peaks at -4.22 and -5.22 eV around the low energy region in Figure 5a. The peak in the high-energy region of the conduction band is attributed to the O-2s contribution. Similarly, the contribution of the Zn-4s and O-2p states leads to the peaks in the valence band. The first peak at 3.29 eV appears in the valence band of Al-ZnO, which is related to the Zn-4s, Al-3s, and Al-3p states. In Figure 5b, the three peaks at -3.56 , -6.59 , and -7.64 eV appear in the low-energy state, which is mainly due to the interaction between O-2p, Zn-3d, Al-3s, and Al-3p states. There is a peak (-19.44 eV) in the high-energy region of the conduction band, which is mainly due to the hybridization between O-2s, Al-3s, and Al-3p states. Compared with metal single doping ZnO (Al-ZnO), the DOS of metal/metal co-doping ZnO (Al/Ag-ZnO) shifts toward lower energy, and the Fermi level moves into the conduction band. In Figure 5c, the peak in the low-energy region of the conduction band is ascribed to the O-2p, Zn-3d, Al-3s, Al-3p, and Ag-4d states. In Figure 5d, for metal/non-metal co-doping ZnO (Al/N-ZnO), the valence band peak at 5.80 eV is related to the Al-3s and Al-3p states. However, N atoms have little effect on the valence band of DOS. The O-2p, Al-3s, Al-3p, and N-2p states cause lower peaks near the Fermi level. Two high peaks occur in the conduction band, which are mainly contributed by the Zn-3d, O-2p, Al-3s, Al-3p, and N-2p states. The energy band

ranging from -16.52 to -18.17 eV is mainly controlled by the O-2s, Al-3s, and Al-3p states. The introduction of the N-2s and N-2p states makes the O-2p states approach the valence band, which decreases the bandgap.

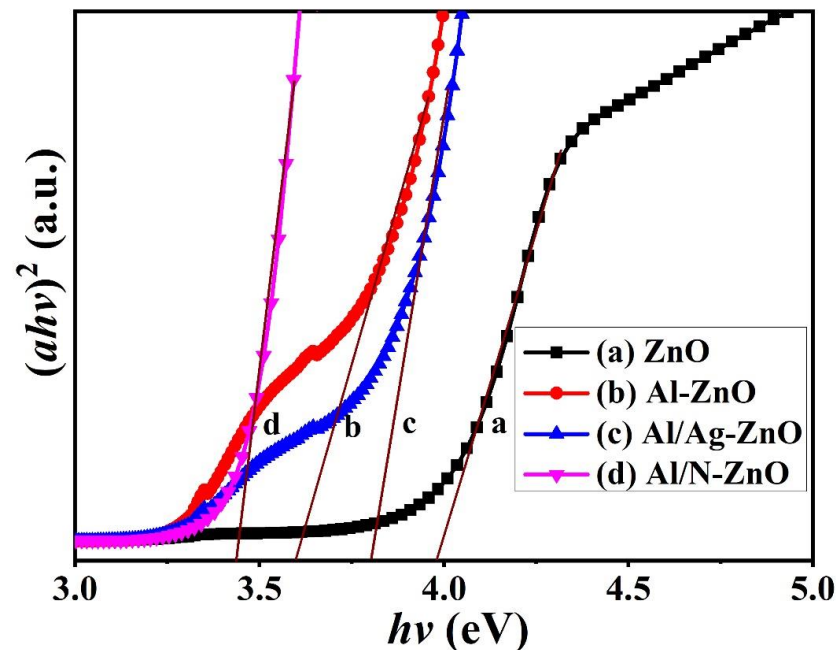


Figure 4. Optical band gap of ZnO (a), metal single doping ZnO (Al-ZnO) (b), metal/metal co-doping ZnO (Al/Ag-ZnO) (c), and metal/non-metal co-doping ZnO (Al/N-ZnO) (d). The brown lines illustrate the method of fitting the linear region to evaluate the band gap at the x-axis intercept.

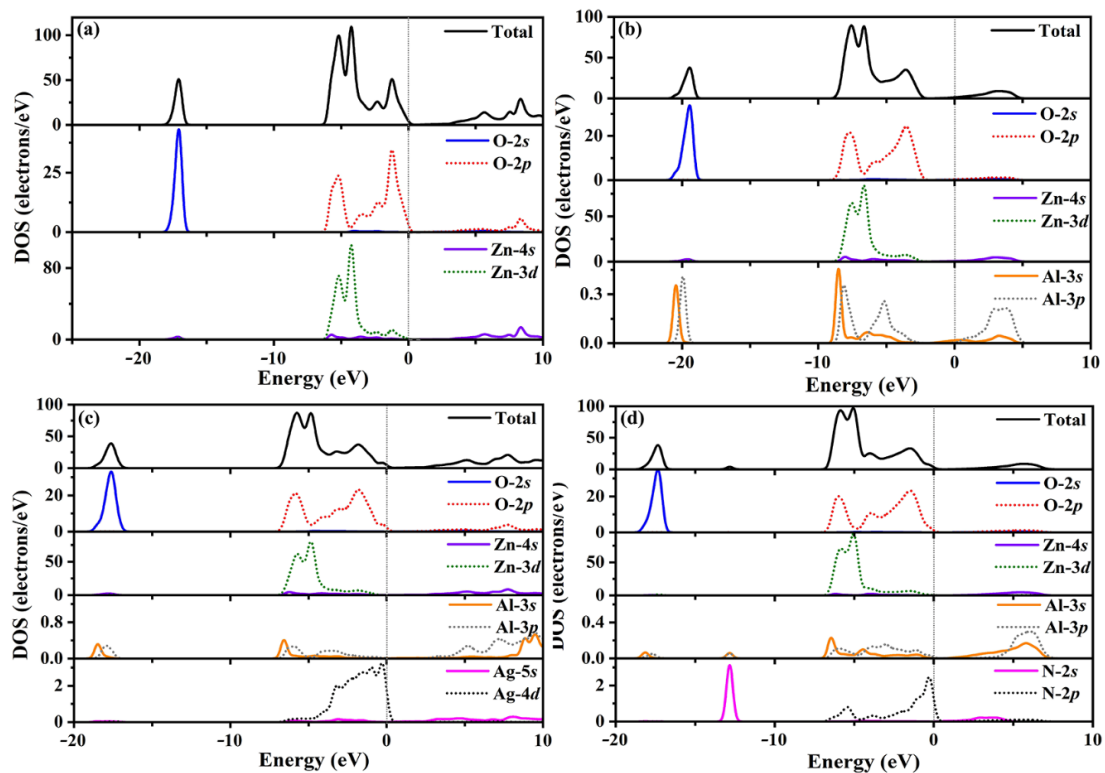


Figure 5. The density of states (DOS) and partial density of states (PDOS) of ZnO (a), metal single doping ZnO (Al-ZnO) (b), metal/metal co-doping ZnO (Al/Ag-ZnO) (c), and metal/non-metal co-doping ZnO (Al/N-ZnO) (d), respectively. The Fermi level is marked by a gray dashed line.

Figure 6a revealed the absorption of pristine and doped ZnO. The peaks in the x, y, and z directions appear at about 3.80 eV, 3.89 eV, and 3.92 eV, respectively. Al/Ag-ZnO has an absorption peak (19.95~21.24 eV), indicating that the light absorption is enhanced after metal/metal co-doping. The maximum peak of the total absorption coefficient is observed at around 14.23 eV, while the total absorption peak is at 2.90 eV. The energy-loss function is another important optical constant, which is usually used to evaluate the energy loss of electrons passing through a homogeneous medium. Figure 6b is the energy-loss function for pristine and doped ZnO with the peak at 19.19 eV. This peak reflects the characteristics related to plasma oscillation. For example, the oscillation frequency is the corresponding plasma frequency, and the maximum (or peak) is a multiple of the plasmon energy or frequency. In Figure 6c, the refractive index almost remains unchanged, especially in higher energy region. The reflectivity of the pristine and doped ZnO is displayed in Figure 6d. If the reflectivity is 1, this indicates that the material exhibits perfect reflectivity. The calculated reflectivity of Al-ZnO at 0 eV (surface) is 0.33, which shows that Al doping improves the reflectivity of ZnO.

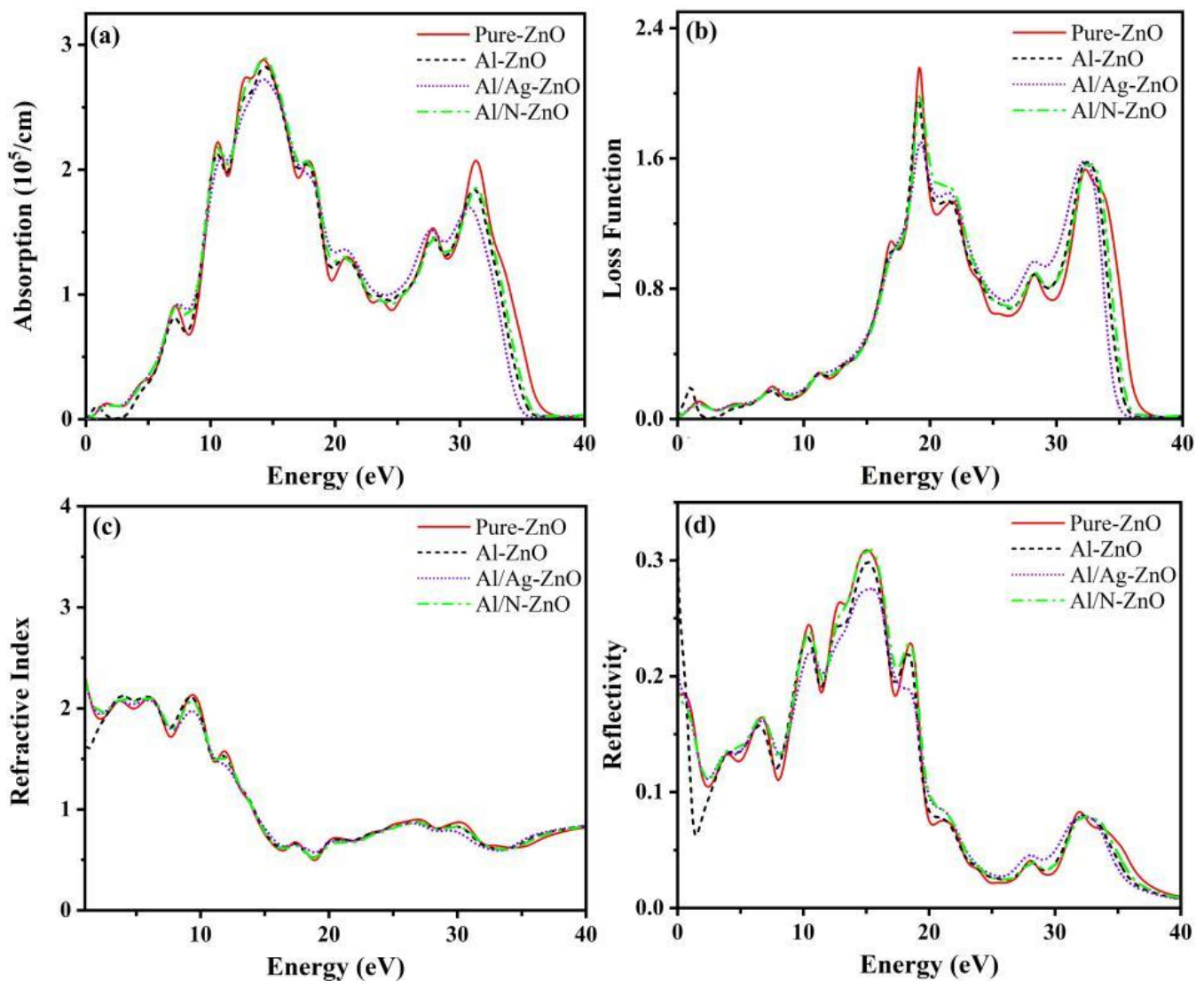


Figure 6. Optical constants of doped ZnO, including absorption (a), loss function (b), refractive index (c), and reflectivity (d).

Figure 7 depicts the PL spectra of ZnO (a), metal single doping ZnO (Al-ZnO) (b), metal/metal co-doping ZnO (Al/Ag-ZnO) (c), and metal/non-metal co-doping ZnO (Al/N-ZnO) (d). The PL excitation source wavelength and the temperature regime are 325 nm

and room temperature, respectively. The PL spectrum of ZnO shows a violet emission peak at 406 nm and other weak visible emission peaks. After Al doping, a strong blue emission peak at 421 nm is observed, and its intensity is further enhanced and attains the maximum for Al/N-ZnO. However, for Al/Ag-ZnO, the blue emission shifts toward a longer wavelength, and the intensity of the blue emission conversely decreases. Different researchers proposed different hypotheses about the origin of PL emissions related to defects, but so far, there is no consistent conclusion. For blue light emission in particular, its origin has always been the focus of debate among researchers because of its sparsity and instability. For example, Guo et al. [24] constructed type II band structures based on ZnO nanowire arrays and discussed their potential applications in photodetectors. Kang et al. [25] prepared nickel-doped ZnO electrodes for blue light-emitting diodes. Khokhra et al. [26] found that the visible light photo-detection capability of the ZnO nanostructure greatly depends on its morphologies. Ghosh et al. [27] fabricated ZnO-based heterojunction and discussed the emission mechanism of both the blue-violet and blue emission peaks.

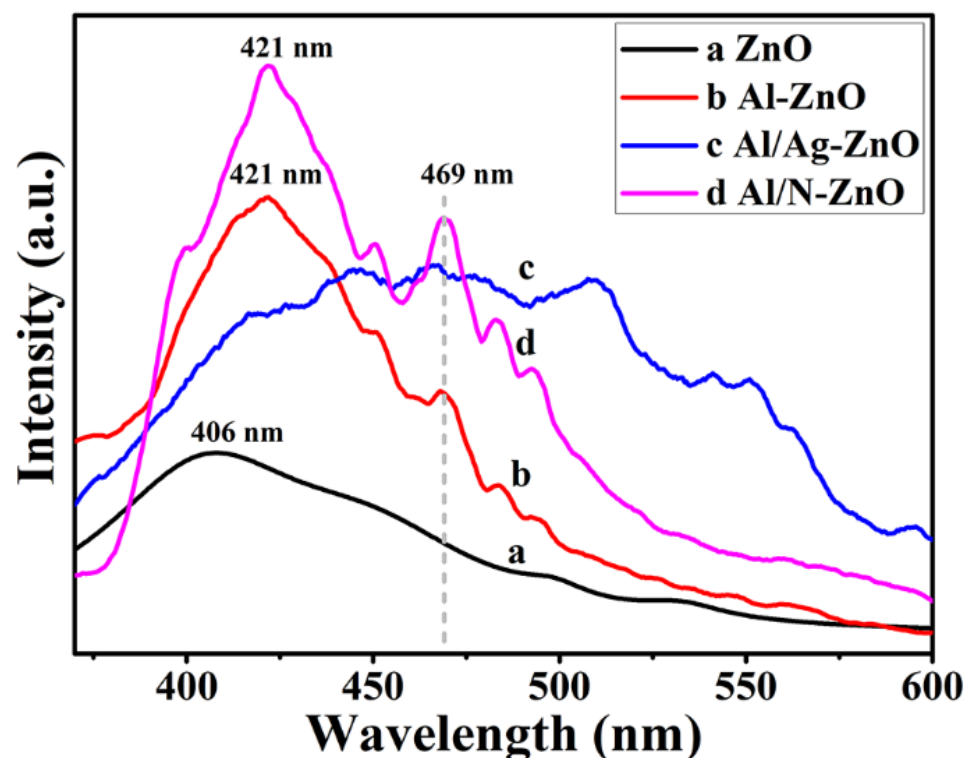


Figure 7. PL spectra of ZnO (a), metal single doping ZnO (Al-ZnO) (b), metal/metal co-doping ZnO (Al/Ag-ZnO) (c), and metal/non-metal co-doping ZnO (Al/N-ZnO) (d).

In this work, the violet peak of ZnO has a redshift to the blue band after metal Al single doping ZnO, which is considered to be related to the change of ZnO bandgap. At the same time, the intensity of the blue emission rapidly increases after Al and N co-doping, and sharp quenching in the case of Al and Ag co-doping. Both metal/metal and metal/non-metal co-doping are highly non-equilibrium processes. Generally, a large number of defects will occur, and interstitial zinc defects are dominant in the as-prepared ZnO films. In addition, among the four samples, the bandgap of Al/N-ZnO is the smallest, which makes the optical transition easier, so the optical properties of ZnO are also improved.

4. Conclusions

ZnO, metal single doping ZnO (Al-ZnO), metal/metal co-doping ZnO (Al/Ag-ZnO), and metal/non-metal co-doping ZnO (Al/N-ZnO) are deposited. Crystal structures, band structures, DOS, PDOS, optical constant, and PL properties are investigated by theoretical calculation and experimental characterization. The results show that different doping

leads to the change of the (002) peak intensity, which reaches the maximum for Al and N co-doped ZnO. In addition, the PL spectrum of ZnO shows a violet emission peak at 406 nm and other weak visible emission peaks. After Al doping, a strong blue emission peak at 421 nm is observed, and its intensity is further enhanced and attains the maximum for Al/N-ZnO. However, for Al/Ag-ZnO, the blue emission shifts toward a longer wavelength, and the intensity of the blue emission conversely decreases. Comparing the four samples, the bandgap of Al/N-ZnO is the smallest, which facilitates electronic transitions from the valence band to the conduction band and improves the optical properties of ZnO.

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