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# Effects of Ga concentration on electronic and optical properties of Ga-doped ZnO from first principles calculations

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ABSTRACT

This study evaluated the electronic and optical properties of Ga-doped ZnO with various concentrations of gallium, employing first principles calculations based on density functional theory and the Hubbard U (DFT + $U_d$ + $U_p$). The lattice constants and band gap of ZnO calculated in this study are in agreement with experimental values. Results show that donor concentration increases with an increase in Ga concentration; however, electrical conductivity is reduced when localized states close to the Fermi level and higher scattering probability of free electrons occur with high Ga concentration. Following the incorporation of Ga into ZnO (1.4–6.3 at.%), the average transmittance of light in both the visible and UV ranges exceeds that of ZnO. However, the stronger and wider donor states obtained from high doping levels (12.5–25 at.%) significantly decreases the average transmittance. Thus, selecting a suitable doping level is crucial to optimizing the photoelectric performance of Ga-doped ZnO. This study also provides a theoretical explanation for the factors influencing these properties.



## 1. Introduction

ZnO-based materials have considerable potential in transparent conductive oxides (TCOs) due to their wide band gap (3.37 eV) and transparency under visible light. The presence of intrinsic defects including oxygen vacancies or interstitial Zinc atoms causes ZnO to exhibit n-type conduction [1]. ZnO can also be applied to light emitting devices due to its large binding energy of 60 meV [2,3]. Although interstitial Zinc atoms can form shallow donor states and supply conductive electrons, these interstitial atoms tend to be unstable due to a low diffusion barrier [4]. According to first principles calculations, the deep donor states formed by oxygen vacancies are incapable of supplying conductive electrons at room temperature [5]. Therefore, a suitable dopant is necessary for the application of ZnO–TCOs.

Among the available metal dopants, Ga [6–10], Al [11], and In [12] have received particular attention. Unfortunately, the toxicity of In and its effects on humans and the environment have also attracted a great deal of concern [13,14]. When the Al content exceeds 3 at.%, interstitial Al atoms are easily formed, which generates localized gap states. As a result, the resistivity of Al-doped ZnO does not decrease continuously [15,16]. Ga incorporated into ZnO (GZO) is believed to have considerable potential due to its low Madelung energy [17] and ionic radius, which lies in between $Ga^{3+}$ (0.62 Å) and $Zn^{2+}$ (0.74 Å) [9], and therefore reduces lattice distortion. Doping ZnO with Ga has been shown in experiments to decrease resistivity to the order of $10^{-4}\,\Omega\,cm$ and increase transmittance to above 90% [6]. Additionally, the effects of Ga concentration on the photoelectric properties of GZO have been widely reported [7–9]. Zhao et al. [7] showed that a low resistivity of $3.6 \times 10^{-4}\,\Omega\,cm$ and transmittance above 90% (averaged over the visible region), can be obtained at an optimal Ga concentration of 4.9 at.%. When the Ga content was increased to 10.5 at.%, the optical band gap also increased, resulting in a blue shift in the absorption edge. Shinde et al. [8] also observed a blue shift following an increase in Ga content from 0 to 5 wt.% as well as increased transmittance at wavelengths shorter than 350 nm. Tsay et al. [9] demonstrated that the average transmittance of GZO thin films exceeds 91% when the concentration of Ga exceeds 2%, reaching maximum transmittance at 92.1% with a Ga content of 3%.

In recent years, many studies have adopted first principles calculations to investigate the effects of doping on various properties of ZnO, such as crystal structure, electronic characteristics, and optical properties [18–23]. These theoretical calculations can provide considerable insight into the microscopic characteristics of these materials, which could assist with the future design of materials. However, standard density functional theory (DFT) underestimates the band gap of many transition metal oxides and ZnO is

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no exception. For example, the calculated band gap of ZnO was found to be only 0.81 eV, which is considerably less than the experimental value of 3.37 eV [22]. Although the DFT + $U_d$ (the correction is only applied to transition metal d orbitals) method has been successfully used to correct the band gap for some transition metal oxides [24,25], the calculated band gap for pure ZnO was still underestimated [21–23]. For example, the calculated band gap obtained using DFT + $U_d$ was found to be approximately 1.5 eV [21]. To obtain a more accurate representation of the electronic structure of transition-metal oxides, a number of recent theoretical studies have investigated the influence of the Hubbard U parameter on the p orbital electrons of oxygen ($U_p$) and the d orbital electrons of the transition metal ($U_d$). Ma et al. [26] adopted both $U_p$ and $U_d$ values in $Ag_3PO_4$ crystal and the calculated parameters for structural equilibrium were in excellent agreement with experimental values, with a deviation of only 2% in the lattice constants. In another calculation model, Sheetz et al. [27] indicated that the correct band gap of ZnO can be obtained using $U$ values of $U_{d,Zn}$ = 10.5 eV for Zn 3d and $U_{p,O}$ = 7.0 eV for O 2p.

To the best of our knowledge, few studies have focused on the electronic structure and optical properties of Ga-doped ZnO (GZO) with various concentrations of Ga. This study performed first principles calculations using the DFT + $U_d$ + $U_p$ approach to investigate the crystal structure, formation energy, electronic structure, and optical properties of $Zn_{1-x}Ga_xO$. Analysis was performed using Ga concentrations of, 1.4, 3.1, 6.2, 12.5, and 25 at.%.

## 2. Calculation models and methods

In our preliminary calculations, the formation energy of interstitial Ga far exceeded that of substitutional Ga in ZnO; interstitial Ga doping was not considered in this study. To simulate various concentrations of Ga, this study considered $3 \times 3 \times 2$, $2 \times 2 \times 2$, $2 \times 2 \times 1$, $2 \times 1 \times 1$, and $1 \times 1 \times 1$ supercells, in which one Zn atom is substituted with one Ga atom, corresponding to doping levels of 1.4, 3.1, 6.2, 12.5, and 25 at.%, respectively. Although the GZO with 25 at.% Ga cannot be reached in real samples, it can be used as a reference to the qualitative analysis of the high Ga concentration.

CASTEP code 5.5 [28] was employed to calculate the structural, electronic and optical properties using first principles calculations based on density functional theory (DFT) with plane-wave pseudopotentials. Vanderbilt-form ultrasoft pseudopotentials [29] with valence electron configurations of $4s^23d^{10}$ for Zn, $2s^22p^4$ for O, and $4s^23d^{10}4p^1$ for Ga were used to describe the interactions between the ionic core and valence electrons. The electron wave functions were expanded through a plane wave basis set and the cutoff energy was selected as 380 eV. For k-point sampling, we used a $4 \times 4 \times 2$ Monkhorst–Pack grid in the first Brillouin zone [30]. The convergence threshold for self-consistent iteration was set at $10^{-4}$ eV/atom, and the lattice constants and all atomic positions for each supercell were fully relaxed until the maximal force on each atom was less than 0.03 eV/Å, the internal stress was below 0.05 GPa, and the displacement of each atom was below 0.001 Å.

To describe the electronic structures accurately, we adopted the DFT + $U_d$ + $U_p$ method. Ma et al. [26] suggested that for oxide materials the $U_{p,O}$ value of 7 eV is suitable for first principles calculations. Therefore, both $U_d$ values for Zn 3d and the $U_p$ value for O 2p were considered with $U_{p,O}$ fixed at 7 eV in our calculations. Fig. 1 shows the relationship between the energy band gap and $U_d$ values, where $U_d$ ranges from 0 to 12 eV. The value for the band gap is smaller than the experimental value at $U_d$ = 0 eV. The band gap increases with an increase in $U_d$ in the range from 0 to 10 eV. When $U_d$ = 10 eV, the calculated band gap and lattice

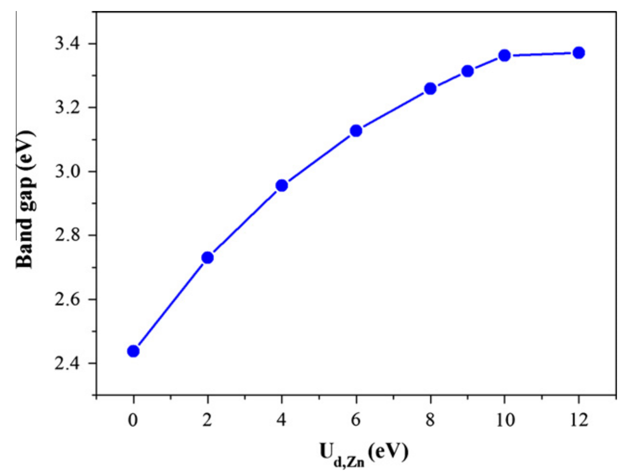


**Fig. 1.** Band gap of ZnO as a function of $U_{d,Zn}$ parameter with $U_{p,O}$ fixed at 7 eV.

parameter a of pure ZnO are 3.37 eV and 3.258 Å, respectively. These results are in excellent agreement with experimental values. Therefore, we adopted $U_{p,O}$ = 7 eV and $U_{d,Zn}$ = 10 eV for this study.

## 3. Results and discussion

### 3.1. Structural optimization

Table 1 lists the lattice constants, differences in volume, and average Mulliken charge for GZO at various Ga concentrations for the optimized structure. The optimized lattice constants of pure ZnO were $a = b$ = 3.25 Å and $c$ = 5.232 Å. The deviation in lattice constant between the calculated and experimental values ($a = b$ = 3.25, $c$ = 5.207 Å [31]) was less than 1%, indicating that our calculations are reliable. This study found that, although the radius of $Ga^{3+}$ (0.62 Å) is smaller than that of $Zn^{2+}$ (0.74 Å), the volume of the crystals expands following the incorporation of Ga into ZnO and increases with an increase in Ga concentration. The example in Fig. 2 (with a concentration of 1.4 at.%) illustrates the reason for this expansion in volume. At a Ga concentration of 1.4 at.% (Fig. 2), Mulliken population analysis shows that Ga has a stronger positive charge (1.38) than Zn (0.93), and the variation in Mulliken charge for O is not obvious compared with pure ZnO (Table 1). This means that the Ga dopant contributes more electrons than Zn. Therefore, the Coulomb attraction between Ga and O ($|(1.38)(-0.94)|$) is larger than between Zn and O ($|(0.93)(-0.94)|$), resulting in Ga–O bond lengths that are shorter than Zn–O bond lengths (Fig. 3). However, extended Zn–O bonds make up the majority, resulting in an expansion in volume. With an increase in Ga concentration from 1.4 to 25 at.%, the average Mulliken charge of Zn and Ga decreases; meanwhile, the charge of O slightly increases, resulting in weaker Coulomb attraction for Zn–O or Ga–O. The weaker Coulomb attraction leads to an

**Table 1**
Optimized lattice constants, difference in volume ($\triangle V$), and Mulliken charge of ZnO doped with various concentrations of Ga.

| Ga concentration (at.%) | $a$ (Å) | $c$ (Å) | $\triangle V$ (%) | Mulliken charge $\|e\|$ | | |
|---|---|---|---|---|---|---|
| | | | | Zn | O | Ga |
| 0 | 3.250 | 5.232 | – | 0.94 | −0.94 | – |
| 1.4 | 3.252 | 5.243 | 0.32 | 0.93 | −0.94 | 1.38 |
| 3.1 | 3.254 | 5.255 | 0.69 | 0.92 | −0.93 | 1.27 |
| 6.2 | 3.256 | 5.283 | 1.36 | 0.89 | −0.92 | 1.24 |
| 12.5 | 3.261 | 5.318 | 2.74 | 0.86 | −0.91 | 1.10 |
| 25.0 | 3.324 | 5.304 | 5.81 | 0.77 | −0.90 | 1.05 |