Effect of Gallium and Aluminum on the electronic and optical properties of Zn$_{1-x-y}$Ga$_x$Al$_y$O up to (x,y)=(25,12.5)%

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Abstract – We present, in this paper a comparative study of structural, electronic and optical properties of pure ZnO and ZnO co-doped with gallium and aluminum at different concentration Zn$_{1-x-y}$Ga$_x$Al$_y$O up to (x,y)=(25,12.5) %. The calculated structural parameters were obtained using the Generalized Gradient Approximation (GGA-PBE). The electronic structure, the imaginary part of the dielectric function, the absorption coefficient, and the reflectivity were determined using the modified Becke-Johnson potential (mBJ). We have found that these elements present a good optical conductivity with a significant improvement for the ZnO co-doped (Al, Ga) at different concentrations compared to the pure ZnO. The results for pure and co-doped ZnO are in a good agreement with experimental results and other theoretical studies and confirm their usability in photovoltaic devices.

Keywords: DFT, ZnO co-doped Ga-Al, mBJ potential, Electronic structures and Optical properties.

I. Introduction

The zinc oxide (ZnO) has attracted attention as Transparent Conduction Oxide (TCO) because of its large direct band gap of 3.4 eV [1], its n-type conductivity caused by a native defect [2], it’s no toxicity, its terrestrial abundance that makes it inexpensive, also the wide range of its electrical resistivity (ranging from $10^{-4}$ to $10^{12}$ Ω.cm depending on the deposition conditions [3]), and therefore an attractive material for optoelectronic applications [4,5]. A variety of techniques have recently been introduced in an effort to improve optical and electrical properties for ZnO-based TCOs. Especially, codoping with solute atoms is an effective method to improve various properties of ZnO for TCO. In singly-doped ZnO, Ga-doped ZnO (GZO) has attracted much attention as a promising solution to realize electrical and optical performing transparent conductive oxide TCO layer, as Ga is an n-type dopant in ZnO that increases the carrier concentration and hence the conductivity of the layer [6-10]. In the same way, Al-doped ZnO (AZO) layers and films have attracted the attention of most researchers for many advantages in terms at first, of high conductivity and thermal and chemical stabilities [11-13], at second, its relative high abundance of the elements constituting the compound and their low toxicity, and, finally to the possible production of films or layers at low cost. In comparison, Ga-doped ZnO (GZO) films have low durability in moist environment and are more expensive to produce than AZO films [14].

Thus, it appears that codoping with Al and Ga is attractive because an improvement in performance can be expected in various properties. However, few studies on ZnO co-doped Ga-Al (AGZO) are reported in the literature [15-17]. Therefore, we investigated the electronic and optical properties of Al-Ga codoped ZnO films with different concentrationZn$_{1-x-y}$Ga$_x$Al$_y$O starting from pure ZnO (x=y=0) and with the following ones (x=25%, y=0%); (x=18.75%, y=6.25%); (x=y=12.5%), using the linearized augmented plane wave method and the generalized gradient approximation (GGA) based on density functional theory (DFT).

II. Computational method

As a computational tool, we have employed the full-potential linearized augmented plane-wave method (FP-LAPW) based on density functional theory (DFT) using the WIEN2K package [18, 19]. The exchange
and correlation energy was described by generalized gradient approximation within the Perdew–Burk–Ernrenhof PBE-GGA parameterization [20] for structural calculations, and Tran–Blaha-modified Beck and Johnson TB-mBJ approximation [21] for electronic and optical properties calculations. The convergence test calculation has shown that for pure ZnO and Al and Ga co-doped ZnO, 100 k-points and 75 k-points, respectively in the irreducible part of the Brillouin zone are sufficient to minimize with a satisfactory accuracy the total energy. The radii of the muffin-tin atomic spheres RsMT of Zn, Al, Ga and O atoms are 1.84, 1.67, 1.81 and 1.58 a.u., respectively. The cutoff parameter RsMT×Kmax are 8.5 and 7, for ZnO and AGZO, respectively, where RsMT denotes the smallest muffin-tin radius of atoms and Kmax is the maximum value of the reciprocal lattice vectors used in the plane wave expansion. The convergence of the calculated total energy is reached for values less than 10−6 Ry, which means that the self-consistent calculation is considered as stable. The Fourier charge density Gmax is 1.2 (Ryd)1/2. To show the effect of different couples of dopant concentrations in Zn1-x,y,Ga,x,Al1-y,O, we starting from pure ZnO (x=y=0) and with the following ones (x=25%, y=0%); (x=18.75%, y=6.25%); (x=y=12.5%). We consider the following cases: one Zn atom can be substituted by one Ga atom, two Zn atoms are substituted by one Al atom and one Ga atom, and four Zn atoms are substituted by one Al atom and three Ga atoms. It is to be noted that this behavior was also observed for the GZO in the recent work of H.I Berrezoug et al. [25] and for the AZO in the works of H. C. Wu et al. [22].

III. Results and discussion

III.1. Structural parameters

The hexagonal wurtzite structure with space group symmetry of P63mc (No 186) is the unit cell of ZnO found in nature (normal temperature and pressure). The experimental lattice parameters are a = b = 3.25 Å, c = 5.23 Å, a = b = 90° and c = 120° [22]. In order to get the relaxed lattice parameters, the total energy is, firstly, calculated versus reduced volume and c/a ratio of pure and (Al, Ga) co-doped ZnO in different super-cells. According to these calculations, the relaxed lattice parameters of pure ZnO are a =3.294 Å and c = 5.252 Å, which are close to the experimental ones and in a good agreement with the other theoretical calculations [13, 23].

For (Al, Ga) co-doped ZnO cases, we plot in figure 1, the variation of the lattice constants as a function of (Al, Ga) concentrations for Zn1-x,y,Ga,x,Al1-y,O (x=25%, y=0%); (x=18.75%, y=6.25%); (x=y=12.5%). It is observed from this Figure that, the lattice parameters change nonlinearly with the increasing of Ga concentration (x) and decreases proportionally with the decreases of Ga concentration(x), as also observed in the other works [15, 16, 24]. This means that (Al, Ga) doping leads to a mismatch. These deviations in lattice parameters are mainly related to the difference in the atomic radius and electron negativity between the Al, Ga and Zn atoms. It is to be noted that this behavior was also observed for the GZO in the recent work of H.I Berrezoug et al. [25] and for the AZO in the works of H. C. Wu et al. [22].

![Figure 1. The variation of the lattice constants as a function of (Al, Ga) concentrations for Zn1−x−y,Ga,x,Al1−y,O (x=25%, y=0%); (x=18.75%, y=6.25%); (x=y=12.5%).](image)

III.2. Band structure and density of state

The band gap energy of a material provides an insight into the optical and transport behaviors of that material and demonstrates various allowed carrier excitations. So to investigate such quantity, we compute the band structures along the principal high symmetry directions in the Brillouin zone (BZ) of pure and Al doped ZnO cases. The electronic band structures of the Zn1-x,y,Ga,x,Al1-y,O compounds are shown in figure 2. The calculated band structure of pure ZnO shows that the minimum of the conduction band and the maximum of the valence band lie at the same k-point (Γ) in the Brillouin zone, confirming that the ZnO is a semiconductor with a direct band-gap. Following the mBJ potential, this band-gap was found equal to of 3.27 eV, which is in a good agreement with the experimental value [26, 27].

Now, when the (Al, Ga) are co-doped in ZnO at different concentrations, the Fermi level move s upward into the conduction band (see fig. 2(c) and (d)), indicating that the compound is a degenerate n-type semiconductor, this is related to a pronounced Burstein–Mott-effect [28,29] which can considerably extend the apparent optical band gap.

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It is clear from the figure that this behavior of Fermi level is more pronounced in the AGZO compounds than in the GZO ones. The calculated optical band gap energies of pure ZnO and (Al, Ga) co-doped ZnO at different concentration are present in table 1. As an interesting result here, is that the incorporation of Al in GZO increases the energy band gap that will be explained from the detailed density of states in the following subsection.

<table>
<thead>
<tr>
<th>x (%)</th>
<th>y (%)</th>
<th>Optical band gap $E_g$ (eV)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>3.27</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>4.33</td>
</tr>
<tr>
<td>18.75</td>
<td>6.25</td>
<td>4.54</td>
</tr>
<tr>
<td>12.5</td>
<td>12.5</td>
<td>4.56</td>
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Table 1. The calculated optical band gap of pure ZnO and (Al, Ga) co-doped ZnO systems at different concentrations.

Figure 3 present the total (TDOS) and partial density (PDOS) of states of Zn$_{1-x-y}$Ga$_x$Al$_y$O at the different concentrations, including the partial of Zn, O, Al and Ga atoms, where the Fermi level is referred to be zero. For pure ZnO (figure 3 (a)), the valence band states are formed by three regions: the first one from $-19.4$ to $-18.7$ eV is principally formed by Zn-4s and Zn-4p orbitals, the second one from $-5$ to $-4$ eV is formed by a sharp and narrow peak of Zn-3d orbital, while the second one above $-4$ eV consists mainly of O-2p orbital. When (Al, Ga) co-doped ZnO at different concentrations, the TDOS of Zn$_{1-x-y}$Ga$_x$Al$_y$O moves, in its entirety, towards the low energy compared to its behavior in the pure ZnO (shown in figures 3(b), (c) and (d)). This indicates why the Fermi level in the band structure moves upward in the conduction band as shown above, thus exhibiting the characteristic of n-type doping. The valence band of AGZO compounds is divided into three regions: i) the upper valence band from $-10.49$ to $-4.69$ eV eV is formed by Zn-3d states, compared with pure ZnO, the substitution process occurring in AGZO lead to a displacement of the optical absorption edge to the UV range. This can be seen through the possible electronic excitations from the valence O-2p states to the conduction Ga-3d states at (x=25% , y=0%) figure 3 (b), and to the conduction Al-3p and Ga-3d states at (x=18.75 %, y=6.25%) and (x=y=12.5%) figure 3 (c) and (d), respectively. ii) The medium valence band ranged between $-20$ eV and $-15$ eV formed by a sharp peak of Ga-3d states, which moves towards higher energy with the decrease of the concentration of Ga (figure 3). We observed also an additional peak corresponding to the O-2s and O-2p states for x=y=12.5% (figure 3.d); iii) The lower valence band ranged between $-25$ eV and $-20$ eV formed by O-2s and Ga-3d states in compound (x=18.75 %, y=0%) figure 3(b), and by O-2s, Ga-3d and Al-3p states in compounds (x=18.75%, y=6.25%) and (x=y=12.5%) as illustrated in figure 3(c) and (d), respectively.

We find also that, the Al-3s, Ga-4s, Zn-4s and O-2p states contribute to the conduction band near the Fermi level. According to the PDOS, the value of the Ga-4s states at Fermi level is relatively important, and contributes significantly to the TDOS of AGZO. These donor states around the Fermi level could be considered as the origin of the conductivity that increases with the Ga concentration. The above analysis is verified by the fact that the area of these occupied states which become wider with insertion of Al (see figure 4). However, these occupied states could be considered as an additional barrier which must be overcome before the electrons can pass to the conduction band.

### III.3. Optical properties

In this part, the optical properties of pure ZnO and (Al, Ga) co-doped ZnO at different concentrations can be described by means of the complex dielectric function $\varepsilon (\omega)$, defined as the summation of their real $\varepsilon_1(\omega)$ and imaginary parts $\varepsilon_2(\omega) : \varepsilon(\omega) = \varepsilon_1(\omega) \pm \varepsilon_2(\omega)$. The imaginary part $\varepsilon_2(\omega)$ of the dielectric function has been obtained from the electronic structure calculations, using the following expression [30]:

$$\varepsilon_2(\omega) = \frac{4\pi^2 e^2}{m^2 \omega \epsilon_0} \sum_{ij} \int \{ |M| \}^2 f_i(1 - f_j) \delta(E_f - E_i - \omega) d^3 k$$  \hspace{1cm} (1)

$M$: is the dipole matrix; $i$ and $j$: are the initial and final states respectively; $f_i$ and $E_i$: are the Fermi distribution...
and the energy of electron respectively as a function of the i th state.

Figure 3. Total and partial density of states for Zn$_{1-x-y}$Ga$_x$Al$_y$O: (a) $x=y=0\%$; (b) $x=25\%$, $y=0\%$; (c) $x=18.75\%$, $y=6.25\%$; (d) $x=12.5\%$, $y=12.5\%$.

Figure 4. The calculated occupied states of electrons in the conduction band near Fermi level as a function of (Al, Ga) co-doped ZnO at different concentrations.

The real part of dielectric function $\varepsilon_1(\omega)$ can be extracted using the Kramers–Kronig relation [31]:

$$\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \text{p} \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega')}{\omega^2 - \omega'^2} \, \text{d}\omega'$$  \hspace{1cm} (2)

with p stands for the principal value of the integral.

Indeed, these two parts allow one to determine other optical properties, such as absorption coefficient $\alpha(\omega)$ and the reflectance $R(\omega)$ using the relations as follows [32]:

$$\alpha(\omega) = \sqrt{2} \omega \left[ \varepsilon_1^2(\omega) + \varepsilon_2^2(\omega) - \varepsilon_1(\omega) \right]^{1/2}$$ \hspace{1cm} (3)

$$R(\omega) = \left| \frac{1-n(\omega)}{1+n(\omega)} \right|^2$$ \hspace{1cm} (4)
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The imaginary part $\varepsilon_2(\omega)$ of the dielectric function of pure ZnO and (Al, Ga) co-doped ZnO cases is present in figure 5. In addition, calculate the imaginary part is important to determine the different transitions between occupied states below Fermi level and unoccupied states on top Fermi level due to the photon absorption. From figure 5 and comparing with the calculations of DOS previously seen, it is found that the peak at energy about 3.27 eV of pure ZnO, which corresponds to the band gap value, results from the optical transition between the valence band maximum formed by O-2p states and the conduction band minimum constituted by the mixed states of Zn-4s and Zn-4p. After the (Al, Ga) are co-doped ZnO at different concentrations, a new big peak for (Al, Ga) concentrations is formed at low energy, due to the transition between the Ga-4s or Al-3s donor impurities around the Fermi level to the Zn-4s and Zn-4p unoccupied states in the conduction band. The peaks are increased and shift in low energy with the increase of Al and the decrease of Ga to $(x=18.75\%,\ y=6.25\%)$.

However, these peaks become more enhances with shift to high energy at the same concentration of Al and Ga $(x=y=12.5\%)$. The thresholds, that corresponds to the transition of the electrons from the valence band to the conduction band, shift to higher energy values related to the band gap when Al concentration increases and Ga concentration decreases. In fact, these thresholds correspond to the transition between the valence band and the conduction band. Additionally, the shifted band gap is related to the localized peak at 4.33, 4.54, 4.56 eV for the compounds $(x=y=0\%)$; $(x=25\%,\ y=0\%)$; $(x=18.75\%,\ y=6.25\%)$ and $(x=y=12.5\%)$ respectively, that results from the transition between the valence band and the conduction band.

When the energy is equal to zero, the reflectivity $R(0)$ is equal to $0.05$, $0.20$, $0.20$ and $0.34$ for $(x=y=0\%)$, $(x=25\%,\ y=0\%)$; $(x=18.75\%,\ y=6.25\%)$ and $(x=y=12.5\%)$ respectively.

Figure 6 shows the reflectivity as a function of wavelength of pure and (Al, Ga) co-doped ZnO. It is clear that the pure ZnO has a low reflectivity in the visible and IR regions (less than 0.1%). However, this reflectivity has significantly increased in the IR region just before the edge of the visible region and decreased from the visible region to the UV region. For (Al, Ga) co-doped ZnO at different concentration, the spectrum of reflectivity increased above 470 nm for $(x=18.75\%,\ y=6.25\%)$ and $(x=y=12.5\%)$, and above 530 nm for $(x=25\%,\ y=0\%)$. Indeed, the incorporation of Al and Ga ions in the structure decreased the reflectivity for wavelengths between 280-470 nm, (see figure 6).

Figure 7 present, the optical absorption spectra of pure ZnO and (Al, Ga) co-doped ZnO. It follows from this figure that the absorption coefficient of pure ZnO is low in the visible region, which is in good agreement with experimental thin film studies [33, 34].
When we co-doped the ZnO with (Al, Ga), we notice that these states induce minimal absorption in the IR region, and of Al, the spectrum absorption increases in contrary with the effect of Ga as an increase of Ga concentration decreases of the absorption. In UV region the absorption spectra becomes lower for all concentrations.

IV. Conclusion

In this works, we have studied the effect the Aluminum and Gallium co-doping on structural, electronic and optical properties of zinc oxide $\text{Zn}_{1-x-y}\text{Ga}_x\text{Al}_y\text{O}$, where we considered four co-doped compounds with with Al and Ga concentrations equal to (x=y=0%), (x=25%, y=0%); (x=18.75%, y=6.25%) and (x=y= 12.5%). This study has been done using the DFT + TB-mBJ. It is found that, the calculated fundamental band gap and the lattice parameters of pure ZnO are in a good agreement with the experimental results ones and other theoretical calculations. It is found that, the calculated fundamental band gap and the lattice parameters of pure ZnO are in a good agreement with the experimental results ones and other theoretical calculations. It is also shown that, the incorporation of (Al, Ga) in ZnO increases the optical band edge absorption greater than that of ZnO pure and of Ga-doped ZnO (x=25%, y=0%), which the Fermi level moves upward in the conduction band, indicating that the material studied has an n-type conductivity. Furthermore, this incorporation creates shallower donor states of Al-3s and Ga-4s around Fermi level in the conduction band minimum. Finally, our optical calculations for (Al, Ga) co-doped ZnO, show that the reflectivity is less than 0.05% and decreases with decreasing Ga concentrations and increasing Al concentrations. Thus it begins to increase at wavelengths greater than 470 nm for (x=18.75%, y=6.25%) and for (x=y=12.5%), and greater than 530 nm for (x=25%, y=0%) in the IR region. These features made the (Al-Ga) co-doped ZnO a transparent conductive electrode for optoelectronic device applications.

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References


