Improvement of optical properties of Mg doped ZnO by nanostructuring for applications in optoelectronics

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Abstract
We have studied the structural, optical, electronic and electrical properties of pure and Mg doped ZnO nanosheets compared to bulk ZnO, using the Density Functional Theory (DFT) within the Full Potential Linearized Augmented Plane Wave (FP-LAPW) formalism. The calculated band structure, total and partial densities of states show that the ZnO nanosheet have a large band gap than the other found in the bulk ZnO, which increases with increasing concentration of Mg. The absorption coefficient and optical transmittance show a red-shift after doping ZnO, whereas, the reflectivity and electrical conductivity are reduced. These good optical properties of ZnO nanosheets make it promising in optoelectronic devices, especially in solar cell application.

1. Introduction

Due to their applications in various optoelectronic devices, zinc oxide crystallized in three-dimensional (3D) structures is one of the most transparent oxides studied experimentally and theoretically in recent years. Actually, the successful development of two-dimensional (2D) nanostructures, such as MoS2/MoSe2 is crucially important for their applications in multifunctional integrated photonics and optoelectronics devices [1–3]. Also, ZnO nanosheet [4, 5] as well as BN boron nitride and graphene [6], has a great importance for the construction of devices at the nanoscale. These nanomaterials can be used in energy storage or conversion [7], photocatalysis [8, 9], data storage, and optoelectronics [10] due to the effects of their small thickness and their high surface area/volume ratio. Various methods, such as the carbothermic reduction process [11], magnetron sputtering [12], physical vapor transport (PVT) [13], electrodeposition [4] and pulsed laser ablation [14], have been used to elaborate a few layers nanostructured of ZnO like graphene.

Recently, ZnO nanosheets have been developed on a substrate of Pd (111) confirming the possibility of obtaining honeycomb structure like graphene. However, the synthesis of a monolayer having atoms in the same plane like graphene, has not been performed experimentally. The study of such structure will facilitate the study of other structures, for instance: ZnO nanotubes (1D) by winding, ZnO fullerene (0D) by enveloping, and bulk ZnO (3D) by stacking [15].

The optical, magnetic, mechanical and electrical properties of the bulk ZnO are very different from 2D, 1D and 0D ZnO due to the quantum confinement resulting from the reduction of their dimensions. In the following, we will cite some theoretical work around ZnO-2D. For example Thanayut et al [16], showed that pure ZnO-2D gap energy decreases by applying tensile or pressure stresses, using ab-initio methods. This later is employed by Haneen Ali Rashed to the stability and electronic properties of Si-doped ZnO nanosheet, their results demonstrate that the gap decreases with the increase in number of Si dopant atoms in ZnO nanosheet and the substitutional silicon atoms on oxygen sites slightly prefer to occupy nearest neighbor sites of zinc [17]. While, Chang-Wen et al [18], calculated the electron structure and magnetic properties of p-doped ZnO-2D nanosheet.
by Bore (B), Carbon (C), Nitrogen (N) and Fluorine (F), and showed that these nanosheets exhibit a magnetic behavior.

In this work, we present the calculations of the structural, optoelectronic and electrical properties of pure and Mg doped ZnO nanosheet by compared to those of the bulk ZnO. We emphasize that the study of ZnO nanosheet requires a very powerful calculator. This computational memory constraint requires us to limit ourselves to relatively large doping concentrations.

2. Computational methods

In this study we have used FP-LAPW method; it is among the most accurate methods for performing electronic structure calculations for crystals implemented in the Wien2k code [19]. Based on the generalized gradient approximation (GGA), the space is dividing into two regions, a spherical ‘muffin-tin’ around the nucleus, the radial solutions of Schrödinger equation and their energy derivatives are used as basic functions, and an interstitial region between the muffin tins (MT) where a plane wave expansion is used.

To get good description of electronic and optical properties, we have started by optimizing our structures. Basically, we have relaxed the wurtzite phase of bulk ZnO which characterized by three parameters: volume, ratio c/a and internal parameters u using functional revised Perdew–Burke–Ernzerhof for solids PBEsol [20], the same functional is used to optimize the structures of ZnO nanosheet.

The optical constants are calculated, in this code, using the well-known relation the dielectric function, of the medium at all phonon energies . The real part of the dielectric function follows from the Kramers–Kronig relation:

\[ \varepsilon_1(\omega) = \text{Re} (\varepsilon(\omega)) = 1 + \frac{1}{\pi} \int_0^\infty \frac{\omega \varepsilon_2(\omega')}{(\omega^2 - \omega'^2)} d\omega' \]

where \( \omega \) stands for the principal value of the integral, and \( \varepsilon_2(\omega) \) is the imaginary part of \( \varepsilon \), which has been obtained directly from the electronic structure calculation.

The absorption coefficient is given by:

\[ \alpha(\omega) = \frac{\sqrt{\pi} \omega}{\varepsilon} \sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2 - \varepsilon_1(\omega)} \]

The reflectivity is calculated to evaluate the percentage of light reflected by studied materials. It makes it easy to obtain the behavior of transparency, and based on the reflectivity, the transmittance has been drawn. The reflectivity \( R(\omega) \) follows directly from Fresnels formula [21, 22].

\[ R(\omega) = \frac{\sqrt{\varepsilon(\omega) - 1}}{\sqrt{\varepsilon(\omega) + 1}} \]

Transport properties such as electrical conductivity are calculated using the Boltzmann theory implemented in the BoltztraP code [23, 24].

3. Results and discussions

3.1. Structural properties

The stable configuration of pure ZnO crystal is the wurtzite structure, which consists of Zn and O planes stacked alternately along the c axis. To obtain the 2D structure of ZnO, we used the optimized structure of this stable structure for which we made a cut along the plane (0001) as shown in figure 1(a), where the O and Zn do not occupy the same plan. The structure obtained is then optimized to obtain the nanosheet of ZnO (2D). Note that after a total relaxation, this structure is transformed into planar honeycomb structure like graphene as shown in figure 1(a), we note the same result in the case of Mg-doped ZnO nanosheet.

The problem that arises when studying ZnO monosheets is the interaction of two successive planes along the c axis, because of the periodicity offered by the system studied using the Wien2k code. To investigate the interaction between ZnO nanosheets optimized for spacing d (figure 2), we calculated the total energy as a function of the gap energy for several nanosheet structures by varying spacing between 5 Å and 15 Å.
The results are summarized in table 1 which shows that above 10 Å, the total energy as well as the gap becomes constant, meaning that for spacing greater than 10 Å, the interaction between nanosheets becomes very negligible and it can be considered that the nanosheet is isolated. Thus, for all our subsequent calculations we adopted a spacing between single sheets of 10 Å.

For the isolated nanosheet, the Zn–O bond length after relaxation of the structure is 1.876 Å. This value does agree with the experimental value which is 1.9 Å [25] and with other theoretical values which are 1.86 Å as reported by Tu et al [26] and 1.9 Å found by Topsakal et al [27]. It should be noted that this bond length is shorter than that of bulk ZnO which is 1.98 Å [28]. Also, the angles formed by the oxygen and zinc atoms in the

| d(Å) | Total energy (eV) | Band gap (eV) |
|------|------------------|---------------|
| 5    | 50878,15961      | 1.041         |
| 8    | 50878,11471      | 1.642         |
| 10   | 50878,11335      | 1.691         |
| 12   | 50878,09974      | 1.690         |
| 15   | 50878,10110      | 1.690         |

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nanosheet structure are coplanar and equal to 120\(^\circ\) showing the sp\(^2\) hybridization. This sp\(^2\) hybridization of the Zn–O bond in the nanosheet is stronger than the sp\(^3\) bond characterizing the tetrahedral bond in the Wurtzite structure and may explain the narrowing of the Zn–O bond in the nanosheet. A similar trend is also observed in the honeycomb structures of graphene, boron nitride and silicon carbon (SiC)\(^{[29]}\).

The primitive lattice vectors of the nanosheet are of a value \(a = b = 3.250\) Å approaching those of the hexagonal Wurtzite of the bulk, whose value is \(a = b = 3.248\) Å. The calculated structural parameters of the nanosheet are significantly larger than those of graphene and the honeycomb structure of boron nitride (BN), because Zn has a greater radius than that of boron atoms, carbon, nitrogen and oxygen\(^{[29]}\).

After doping the ZnO nanosheet by Mg, it was found that the structural parameters have changed a little bit, due to the ionic radii of Zn and Mg which are practically similar. For example, at the Mg concentration of 12.5\%, the lattice parameters change from \(a = b = 3.250\) Å to \(3.255\) Å.

### 3.2. Electronic properties

#### 3.2.1. Density of charge

The GPW method implemented in the CP2K code\(^{[30]}\) is used to calculate the charge isodensity contours of the pure and Mg doped ZnO nanosheets, the results shown in figure 3 indicate a high density of positive charges around the zinc atoms with spherical and non-overlapping contours revealing the ionic character of the Zn–O bond in the case of the nanosheet. The charge transfer from zinc to oxygen was investigated using Mulliken analysis and the results showed that the charge was \(0.49|e|\) around Zn and \(-0.49|e|\) around the oxygen. This charge is lower than that found in the case of bulk ZnO for which we found the charge around zinc and oxygen equal to \(0.55|e|\) and \(-0.55|e|\). This proved that the charge transfer between cation (Zn\(^{2+}\)) and anion (O\(^{2-}\)) is slightly decreased due to the transition from sp\(^3\) hybridization in the wurtzite structure of bulk ZnO up to sp\(^2\) hybridization in the honeycomb structure of nanosheet ZnO. In the case of the Mg doped ZnO nanosheet at 25\%, the Mulliken analysis shows that the Mg has a positive charge of the order of \(1.58|e|\) larger than that around the Zn which is of the order of \(0.50|e|\). This difference is due to the difference in electronegativity between Mg and Zn. We also note that the charge around the oxygen in the Mg doped nanosheet structure is of the order of \(-0.84|e|\) which is larger than of these found in the case of pure ZnO nanosheet. Additionally, we note more particularly that the insertion of the Mg in the ZnO nanosheet makes lose the honeycomb shape of the isodensity contours which are closer to the Mg\(^{2+}\) ion whereas those of the oxygen become more intense and occupy a larger area.

#### 3.2.2. Energy band structure

The calculated band structure along the high symmetry directions \(\Gamma' - M - K - \Gamma\) in the reciprocal space relative to the hexagonal Bravais lattice 2D is shown in figure 4. This structure express that the ZnO nanosheet has a direct gap measured at the \(\Gamma\) point between the maximum of the valence band and the minimum of the conduction band.

With the increase in the concentration of Mg, there is a narrowing of the valence band and the conduction band moves towards high energies that induce an increase in the gap energy. On the other hand, the analysis of the curvature of the conduction bands of the Mg doped nanosheet shows a decrease in this curvature with respect to that of the pure nanosheet. As this curvature is inversely proportional to the effective mass of the electrons, it is deduced that the effective mass of the electrons in the doped nanosheet is greater than the pure. This effective mass itself inversely proportional to the electrical conductivity will make it possible to say that the Mg doped ZnO nanosheet will not improve its electrical conductivity as we have already shown in the case of...
bulk ZnO [31]. The curvature of the energy bands does not show significant variation with the increase in Mg concentration and therefore the electrical conductivity will not change significantly.

3.2.3. Partial and total states density

In this part, we are interested in determining the atomic orbitals contributing to the formation of energy bands of pure and Mg doped ZnO nanosheets. In figure 5, we presented the partial and total states densities of these nanosheets. The energy bands at the top of the valence band comes mainly from the O-2p orbitals, while the bottom of the band is dominated by the Zn-3d orbitals and the bottom of the band by the O-2s orbitals. In the vicinity of the top of the valence band, a hybridization between the Zn-3d and O-2p orbitals, forms a π bond while in the vicinity of the bottom of the conduction band, a hybridization between the O-2s and Zn-4s states forms a σ bond. The same situation occurs for BN-2D and in graphene according to Sahin et al [29] who found that the stability of planar graphene is maintained by π bonds. If we compare the position of the Zn-4s state defining the bottom of the conduction band in the nanosheets and the bulk ZnO, we notice that this state moves towards the high energies, showing that the transition from the bulk to the nanosheet increases the gap energy of ZnO. This shift is closely related to the effect of confinement of electrons in the direction c.

After the Mg doping, we find the same states established in the DOS of pure ZnO-2D in addition to the Mg-3s and Mg-2p states created by the Mg dopant as shown in figure 6. In the vicinity of the top of the conduction band, the hybridization between the O-2p states and the Mg-2p or Zn-3d states will allow the formation of π bonds, whereas in the vicinity of the bottom of the conduction band, the hybridization between the Mg-3s states and the O-2s or O-2p states will form π or σ type bonds. These bonding types maintain the planar geometry of the Mg doped ZnO nanosheet. On the other hand, we note that the state Zn-4s at the bottom of the conduction band moves to high energies with the increase in Mg concentration which induces a blue shift in the gap energy. As for the valence band, there is a narrowing of this band when the concentration of Mg increases as we have reported on the band structure.

The values of the gap energies are determined from the band structure calculated below. The gap energy that we calculated by the PBE-sol functional of the GGA approximation is 1.69 eV. This energy is lower than that calculated by the GW method which is 3.57 eV [32] and also that recently recorded by the GW0 method from the band structure at Γ point of the Brillouin zone, which is 5.64 eV [29]. It is well known that the GGA approximation doesn’t correctly describes the correlation interactions and underestimates the gap of the
material. Then the gap calculated in this study is underestimated but does not affect the tendency as well as the qualitative analysis of the obtained results.

Table 2 illustrates the gap energies calculated for pure and Mg doped ZnO nanosheets at different concentrations compared to those calculated in the case of the pure bulk ZnO and Mg doped ZnO. By analyzing the results, it is noted that the pure nanosheet ZnO has gap energy of 53.28% higher than that of bulk ZnO. In the case of Mg doped ZnO nanosheets, the gap has an energy exceeding that of the doped bulk by almost 50%. This increase in the gap is caused by quantum origin related to the confinement of the electrons in the direction perpendicular to the plane of nanosheet.

3.3. Optical properties
Optical properties including reflectivity, absorption, and transmittance were calculated for bulk and pure nanosheet ZnO and doped Mg at 12.5%, 25%, and 50%. These optical properties have been calculated in the framework of the GGA approximation. The results presented in figure 7 show that the absorption of pure and doped nanosheets ZnO decreases compared to bulk ZnO. We also note that the threshold of this absorption moves towards the short wavelengths with the increase of the Mg concentration following the increase of the gap energy. The optical gaps, calculated from the Tauc relation [33], of the pure and doped ZnO nanosheets shown in figure 7(d) indicate that Mg doping makes it possible to modulate the gap by moving it towards blue light. Similarly, we compared the reflectivity of the two 2D and 3D structures of ZnO (figure 7). We emphasize that nanosheet structures have a lower reflectivity compared to the bulk and that this reflectivity decreases with doping. The results found for reflectivity and absorption predict that nanosheet ZnO will have higher transmittance than bulk ZnO. Indeed, it has been calculated and shown in figure 7 that there is a clear improvement in the level of transmittance for pure and doped ZnO nanosheet compared to that of 3D structures. This level increases as a function of doping in the both bulk and nanosheet. These excellent optical properties of the ZnO nanosheet make it a potential candidate for photovoltaic applications.

3.4. Electrical properties
The electrical conductivity per time relaxation ($\sigma/\tau$) of pure ZnO-2D and Mg doped ZnO at 25% and 50% was calculated using the BoltzTrap code based on semi-classical Boltzmann theory and the results of the electronic structures obtained above. In order to determine the conductivity nature of the doped ZnO 2D structures, we calculated the Seebeck coefficient as a function of the concentration of the charge carriers. The results are presented in figure 8 which shows that the Seebeck coefficient at the Fermi level ($\mu = E_F$) is negative, meaning that the charge carriers are electrons and the electrical conductivity is n-type. Moreover, this coefficient is

Figure 5. Partial and total states densities of pure and nanosheet of ZnO.
reduced in absolute value when the concentration of the charge carriers increases. This trend is also noted in the case of the bulk ZnO.

On the one hand, the electrical conductivity of Mg-doped ZnO decreases with the increase in Mg concentration. On the other hand, it increases linearly with the increase in electron concentration. The electrical conductivity of pure ZnO-2D is greater than to all cases of Mg doped ZnO-2D. This result is in a good agreement with the analysis of the variation of electrical conductivity from the band structures discussed previously. This tendency has been noted also in the case of the bulk Mg doped ZnO in our previous work \[29\]. Moreover, ZnO nanosheet is found more conductor than bulk ZnO according to the confinement effect.

4. Conclusion

In this work, we have studied the structural, electronic, optical and electrical properties of pure and Mg doped ZnO nanosheets that we have compared to those of bulk ZnO. The gap energy found for pure and doped

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**Figure 6.** TDOS and PDOS of Mg doped ZnO nanosheet at 12.5% (a) Valence band (b) and conduction band (c) of the ZnO nanosheet doped at different Mg concentrations.

**Table 2.** Gap energy of bulk and nanosheet ZnO doped at different concentrations of Mg.

| Mg concentration | Structures |
|------------------|------------|
|                  | Bulk ZnO   | Nanosheet ZnO |
| 0%               | 0.79       | 1.691         |
| 12.5%            | 1.003      | 2.081         |
| 25%              | 1.373      | 2.29          |
| 50%              | 1.722      | 2.70          |
nanosheet ZnO is about 50% larger than that of bulk ZnO. Whereas, the absorption and the reflectivity of these nanosheets decrease in favor of their transmittance whose shift threshold towards the blue light with the concentration of the doping. The electrical properties of pure and Mg doped nanosheets ZnO have been studied and consequently it is shown that these structures are characterized by n-type conductivity and that the ZnO doping by Mg weakens the electrical conductivity of ZnO nanosheet. The optical and electrical properties of ZnO nanosheet are promising for its application as an optical window for solar cells.

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