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Study of the Structure and Electronic Properties of the ZnO Monolayer: Density Functional Theory

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Abstract. ZnO has received considerable attention since it has promising applications in electronic devices. Although many studies have explored the potential of ZnO as a promising material, the precise role of geometric in ZnO remains unclear. This study deals with the electronic structure of the ZnO Monolayer using Density Functional Theory (DFT). The DFT was used to investigate the band structure and density of states of the ZnO Monolayer. It is observed that the structural change of ZnO from bulk to monolayer increases the bandgap by 1.84 eV without changes its natural characteristic. Moreover, This study provides information about the properties of the ZnO Monolayer and its potential in electronic and magnetic devices application.

Keywords: DFT, Monolayer ZnO, Band-gap

Introduction

Semiconducting metal oxides have been extensively studied as functional materials for wide applications relating to sustainable development, such as energy conversion/storage [1], environmental remediation [2], and high-performance electronics [3]. Based on simplicity in synthesis, nontoxicity, and relatively low-cost production, ZnO becomes one of the semiconducting metal oxides that have been used in many applied technologies [4]. Due to the fact that ZnO has its uniques properties, huge demand in manufacturing ZnO provides new opportunities for tuning the nano and mesoscale structures of ZnO to extend its applications [5].

In recent years, ZnO nanostructures such as nanowires, nanobelts, and nanorings have been synthesized for electronic devices such as field-effect transistors [6], supercapacitors [7], and gas sensors [8]. Moreover, several studies have also found that the Zn atoms can induce ferromagnetic properties on thin films of ZnO nanowires without doping transition metal atoms, which commonly are harmful to humans. Thus, ZnO semiconductor material can be used in the biomedical field due to it does not have harmful toxins [9].

The potential of ZnO as a promising material still needs to be explored to enhance its performance. One of the techniques that can be used is by modifying the morphology of ZnO into a monolayer structure. However, modifying the morphology in an actual experiment is

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unpredictable and requires many trials and errors. Therefore, we need a simulation approach to predict the resulting morphology in the modification of ZnO. The morphological modification of various materials, especially ZnO, can be predicted using the Density Functional Theory (DFT) simulation method because the obtained calculations are close to the experimental results [10]. In this study, the ZnO Monolayer will be simulated using DFT to analyze the geometry and electronics properties of the material.

Computational Details

The monolayer structure of ZnO was obtained by cutting the bulk structure of ZnO at [0 0 1] orientation (Figure 1). This treatment is consistent with the structure of the ZnO Monolayer, which was experimentally synthesized by Young and Lai [11]. We constructed a periodic (4 x 4) supercell of ZnO Monolayer with a 15 Å vacuum space in all models to avoid interactions between adjacent layers.

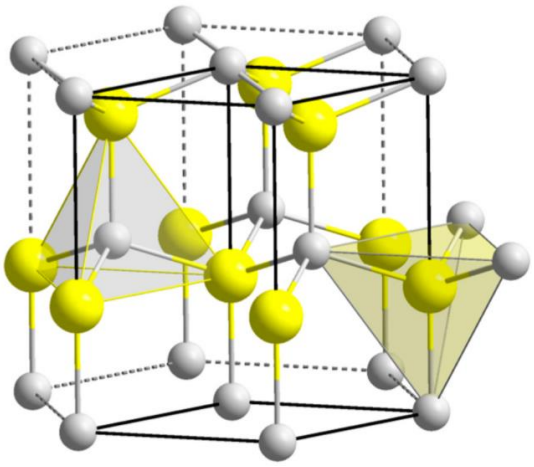

Figure 1. Bulk structure of ZnO; Zn (yellow), and O (grey) [12]

The electronic properties and geometrical structure of the ZnO Monolayer were investigated by the Density Functional Theory (DFT) method. All calculations were performed using Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional implemented in the Vienna Ab initio Simulation Package (VASP) [13]. For the plane-wave basis set, an energy cutoff of 490 eV was used. The maximal force of 0.01 eV/Å was used as the convergence criterion for ionic relaxations, and 10^{-5} was also used for convergence tolerances. The Brillouin Zone was sampled Monkhorst-Pack mesh [14] with 5×5×1 k-points in the geometry optimization and 20×20×1 k-points arranged in the electronic structure [14]. The fully relaxed geometry was performed to obtain the optimized structure. The electronic structure is analyzed by calculating the band structure and the Density of State (DOS).

Results and Discussion

After optimizing the geometry, the layer of ZnO Monolayer changed from the initial structure with a rippled surface into a honeycomb-like structure similar to graphene (Figure 2). Interestingly,

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the calculated Zn-O bond length is 1.876 Å which is shorter than the bulk structure [15]. This result is related to the fact that the atoms in the monolayer structure have a lower coordination number than the bulk structure. Hence, the atoms in the ZnO Monolayer strengthen the bonds between the Zn-O atoms themselves and shorten the bond length.

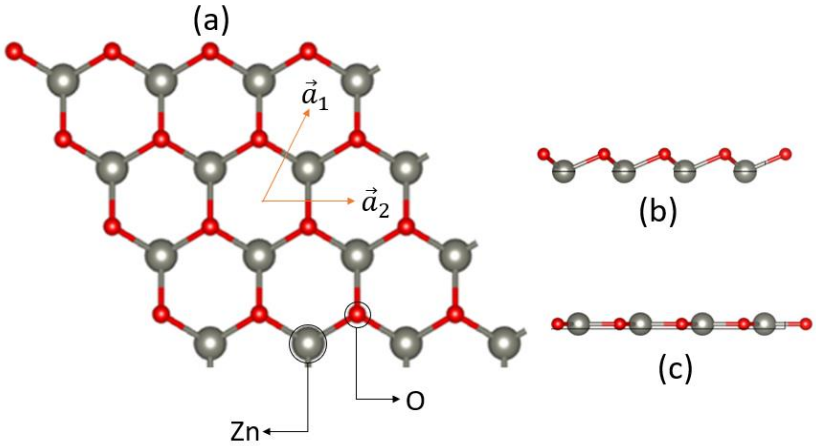

Figure 2. Monolayer Structure of ZnO; (a) Top View; (b) Side View before optimization; (c) Side View after optimization.

To determine the electronic properties of the ZnO Monolayer, it is necessary to calculate the band structure and Density of State (DOS) of the material; the result of the calculation can be seen in Figures 3 and 4.

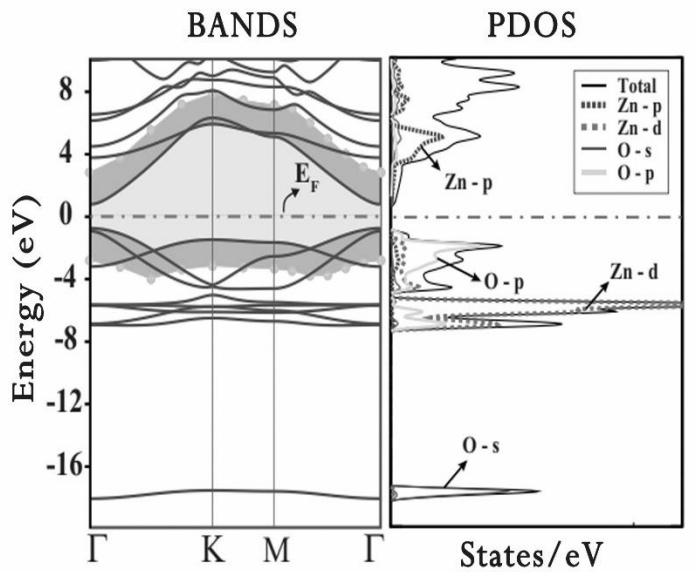

Figure 3. Band Structure and Partial Density of States (PDOS)

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The PDOS in Figure 3 shows that the high density in the conduction band is dominated by O-2p atoms while the valence band is dominated by Zn-3d atoms, which similar to the bulk structure. This result indicates that the Zn atom transfers its charge to the O atom, forming a Zn-O bond with ionic interaction.

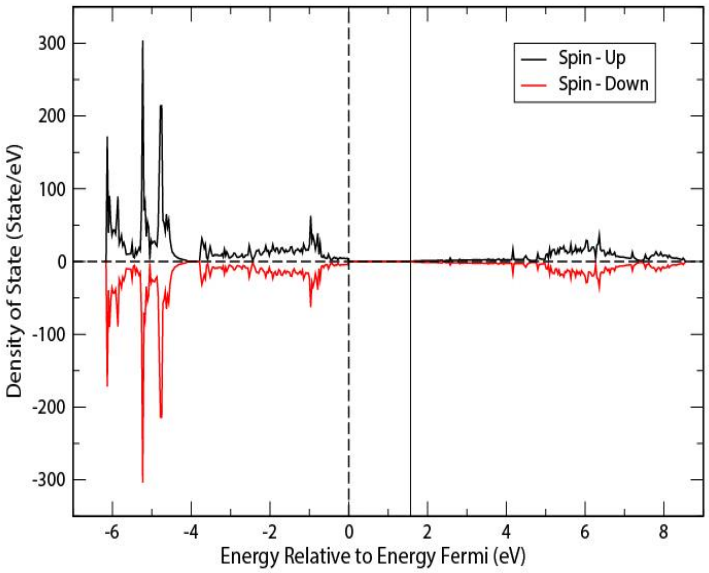

Figure 4. Total Density of States (TDOS)

As shown in Figure 4, the electronic state densities are symmetrical for both spin-up and spin-down. The symmetrical electron density causes the magnetic moment of this material to be zero, indicating that ZnO is a non-magnetic semiconductor material.

Table 1. The Energy Gap of ZnO Materials with Various Nanostructures

Material	Structure	GGA
ZnO	Wurtzite	0.75 eV [16]
	Zincblende	0.65 eV [17]
	Nanowire	0.71 eV [18]
		0.91 eV [19]
	Nanoribbon	1.76 eV [20]
		1.30 eV [21]
	Monolayer	1.84 eV (This study)

In addition, The comparison of the Generalized Gradient Approximation (GGA) bandgap of ZnO semiconductors with various nanostructures is presented in Table 1. The Monolayer ZnO has a direct bandgap of 1.84 eV (Figure 4). This result was higher compared to the other reported nanostructure. The fact also shows that the ZnO Monolayer has a larger bandgap compared to nanowire and nanoribbon structures. The bandgap is the forbidden region to be occupied by electrons. A larger forbidden region signifies a greater restriction on the movement of electrons [22]. Moreover, the large energy bandgap in the UV region and fast recombination rate of

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electron-hole pairs retards its application as a photocatalyst under direct sunlight [23]. These results indicate that Monolayer ZnO can be applied in nanoscale photoelectronic devices, especially for UV photon emitters and detectors.

Conclusions

The structure and electronic properties of the ZnO Monolayer have been investigated using Density Functional Theory (DFT) calculations. The calculation results show that the modification of the ZnO Monolayer structure can provide an alternative to increasing the bandgap without changing the characteristics of ZnO as a semiconductor with a direct bandgap. These results indicate that Monolayer ZnO can be applied in electronic devices such as UV photon emitters and detectors. The DOS analysis also shows that the ZnO Monolayer has a significant charge transfer from the Zinc (Zn) atom to the nearest Oxygen (O) atom.

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