

Electronic properties of zigzag ZnO nanoribbons with hydrogen and magnesium passivations

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ABSTRACT

In this study, the electronic properties of ZnO nanoribbons with zigzag edges (ZZnONr) have been investigated with Density Functional Theory (DFT). After a geometric optimization, the electronic band structures, the density of states (DOS) of ZZnONr passivated with Hydrogen (H) and Magnesium (Mg) atoms were calculated. It is shown that the increasing width of ZZnONrs has led to a decrement in energy band gap of the studied structures. While ZZnONr passivated with Mg for Zn-rich edge have not been shown a spin dependency, the structure passivated with Mg for O-rich edge have exhibited spin-dependent band structure. The energetically most stable structures have been determined as ZZnONr passivated with Mg for Zn-rich edge. ZZnONr passivated with Mg atoms for both edges have a graphene-like band structure especially for 8 and 10 atom width structures and this property of ZZnONrs could be important in terms of the electron transport for ZZnONrs.

1. Introduction

II–VI compound semiconductors have always been an interesting classification of semiconductors due to their possible applications for over a few decades [1,2]. Zinc oxide (ZnO) is a generally n-type semiconductor with a wide band gap (3.37 eV) and a large binding energy of excitons (60 meV) at room temperature [3–8]. ZnO has been successfully investigated in the photonics, optoelectronics, spintronics, and gas sensors applications [9–11]. In addition, ZnO has been regarded as the most suitable candidate for the next generation of ultraviolet (UV) light emitting diode/laser in place of III–V semiconductors [12,13]. ZnO has been studied in a variety of nanostructures including nanowires [14,15], nanorods [16], nanoribbons (Nrs) [17], nanotubes [18,19], nanosheet and bulk structures [20] for both the experimental and the theoretical investigations. Recently, the stability of the graphitic-like structure of ZnO has been studied as both experimentally and theoretically [21–23]. Similar to graphene nanoribbons (GNRs), the different nanoribbon structures have been widely investigated. For example, many experimental and theoretical studies on electronic and structural properties of different nanoribbons including BN [24–26], SiC [27] and ZnO [28–30] have been also reported in details.

It has been theoretically predicted that a single layer ZnO in the honeycomb structure and its armchair edge nanoribbons (AZnONrs) are nonmagnetic semiconductors [30,31], while zigzag edge ZnO nanoribbons (ZZnONrs) show ferromagnetic–metallic behavior [20], which disappears when the edges of ZnO nanoribbons are passivated with hydrogen (H) atoms [32]. Therefore, H passivated ZnO nanoribbons can be important in terms of spintronic investigations. To our best knowledge, the electronic properties of nanoribbons could be changed with doping, edge passivation, applied an electric field to perpendicular-axis of nanoribbons. The electronic band gap can be controlled in these ways. The edge passivation which is one of these ways has been widely used in GNRs [33]. Similar to GNR studies, edge passivation could be considered as controlling electronic properties of ZnO. A theoretical study of the electronic and magnetic properties of pure and 3d TMs (Mn, Fe, and Co)-doped ZnO nanoribbons with armchair and zigzag shaped edges were investigated by Oleg Bovgyra et al. [32].

It is well known that Mg is experimentally used in ZnO studies [34]. Mg-doped ZnO materials have attracted much attention because of their unique UV-luminescent properties based on the radiative recombination of the electron-hole pairs [34]. The bulk ZnO can be alloyed with Mg atoms and MgZnO alloy can be obtained the wide bandgap

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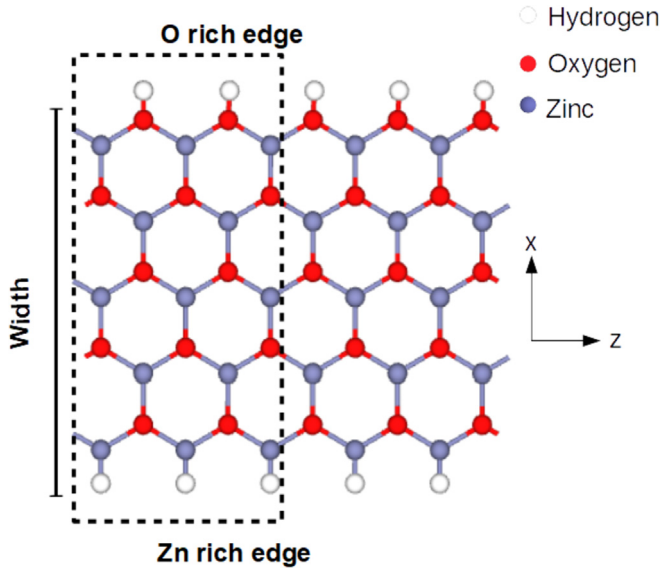


Fig. 1. Atomic configuration of ZZnONrs passivated with H.

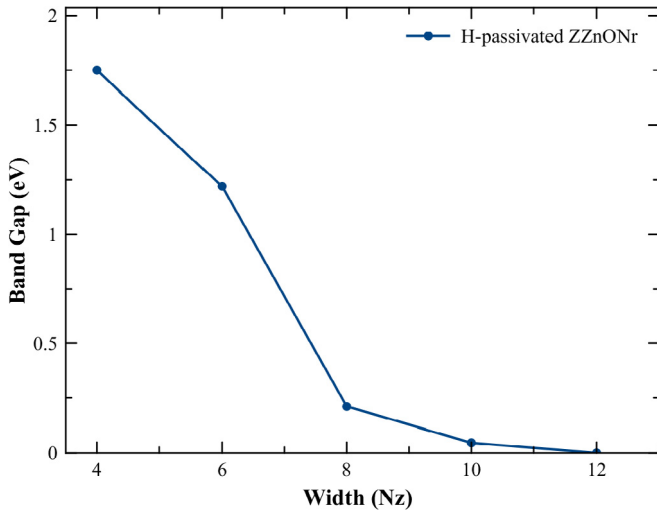


Fig. 2. Electronic band gap values of ZZnONr with H atoms as a function of the ribbon width.

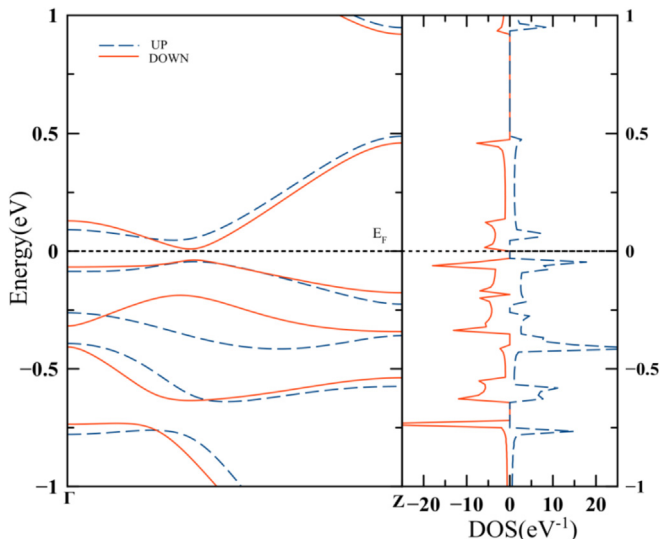


Fig. 3. Electronic band structure and DOS ZZnONr passivated with H atoms.

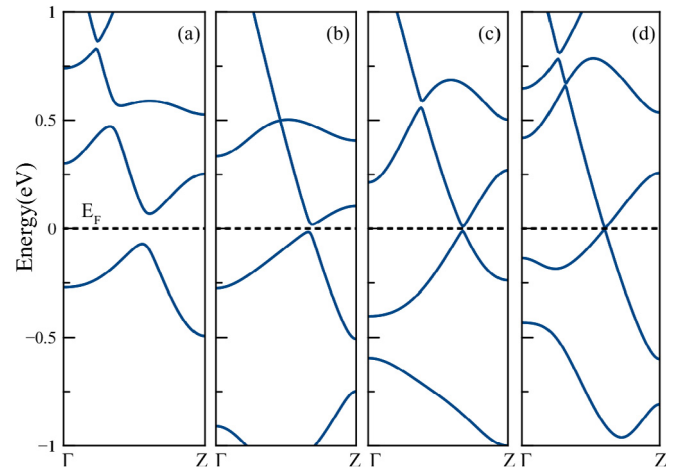


Fig. 4. Electronic band structures of ZZnONr passivated with Mg atoms for Nz = 4–10 atoms widths.

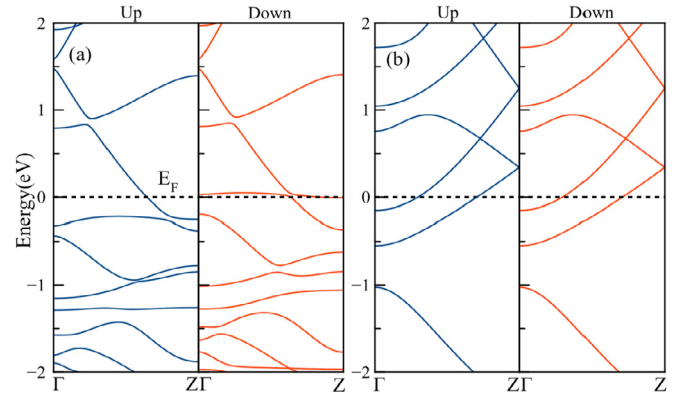


Fig. 5. Electronic band structures for Nz = 10 of ZZnONr with Mg passivation a) for O-rich edge and b) for Zn-rich edge.

semiconductor material changed between 3.3 and 7.8 eV [34]. However, the effect of Mg atom on electronic properties of low dimensional ZnO structures as nanoribbons is still missing.

In this paper, the effect of H and Mg atoms on the electronic properties of ZZnONr have been investigated depending on the ribbon width and the edge passivation by DFT calculations.

2. Numerical methods

All calculations were investigated for ZZnONr passivated with H and Mg having width Nz = 4 to 12. All calculations were carried out based on DFT by the Atomistix-ToolKit Virtual NanoLab (ATK-VNL) software [35]. Spin-polarized Generalized Gradient Approximation (GGA) in these calculations has been studied as an exchange-correlation potential. The cut-off energy and suitable k-point meshes for the Brillouin zone were used 36.75 Rydberg and $1 \times 1 \times 100$, respectively and the applied force to the nanoribbons was used less than 0.01 eV/Å. The electronic behaviors of ZZnONr were studied for different ribbon widths and for passivating with H and Mg atoms. In Fig. 1 atomic configuration of studied ZZnONr was shown.

The ribbon is periodic in the 'Z' direction with the width is illustrate by 'X' direction. The electronic band structure, the total and partial DOS (PDOS) structures of ZZnONr were investigated in details. In order to determine energetically favorable one among the investigated structures, the formation energy (E_F) calculations of each structure have been performed. E_F has been calculated using Eq. (1) [36].

$$E_F = E_T + mE_H - (E_{T,H} + mE_{Mg}) \quad (1)$$

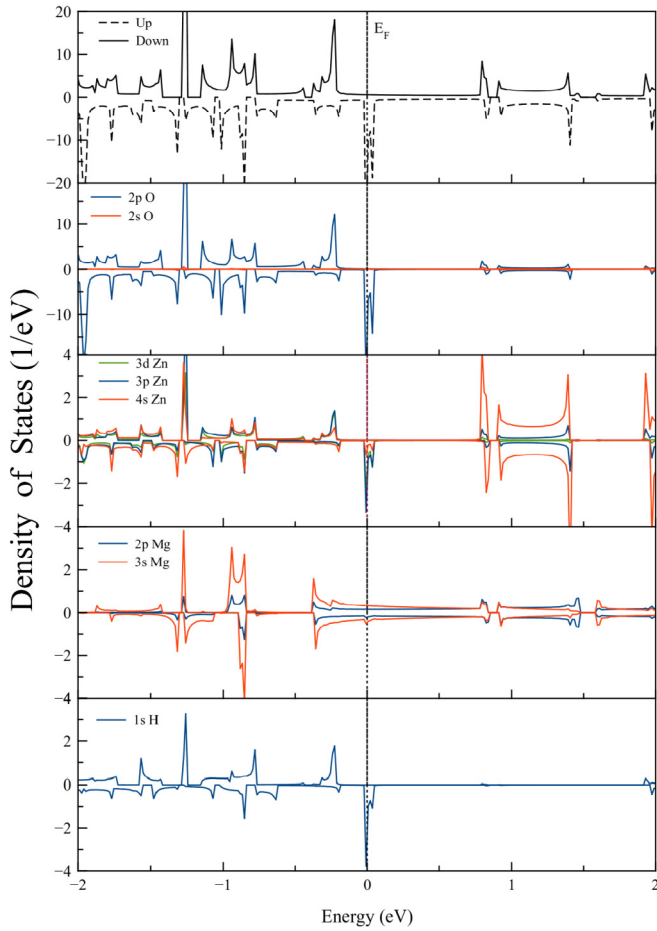


Fig. 6. Total DOS and PDOS of ZZnONr passivated with Mg for O-rich edge.

where E_T , $E_{T,H}$, E_H and E_{Mg} are total energies of passivated structures, H-passivated structures, isolated H and Mg atoms, respectively. Also n and m are number of H and Mg atoms.

3. Results and discussion

The electronic structures of ZnO nanoribbon have a semiconductor behavior and can exhibit magnetic property when ZnO ribbons are passivated with H [29]. Firstly, ZZnONr passivated with H atoms for both edges have been studied depending on the width of ZZnONr. The electronic bandgap is decreased with increasing width of ZZnONr as shown in Fig. 2 similar to Chen et al.'s study [37]. In GNRs, there is a similar behavior between width of nanoribbon and electronic band gap values. Narrow nanoribbons exhibit a larger electronic band gap because of quantum-confinement effects [38]. Also, as increase width of nanoribbons, the interaction between the edges of nanoribbon is decreased and hence this leads to a decrement in band gap of nanoribbon [32].

Experimentally, the different band gap energy has been obtained for different width of ZnO nanoribbons. For example, 3.32 eV, 3.26 and 3.22 eV of band gap have been determined in width of 50–150 nm, 300–500 nm and 2–3 μm of ZnO nanoribbons, respectively [39–41]. According to experimental results, it is shown that the increasing width of ZnO nanoribbons have led to increase band gap of ZnO nanoribbon. In the calculations, the spin-polarized calculations have been performed to investigate the spin dependency as a function of the studied ZZnONr's widths. It is observed that there is no spin dependence in 4, 6 and 8 of the width of ZZnONrs. For 10 atom width of ZZnONr, however, the spin-dependent electronic band structures have been obtained. These results indicate that spin properties of ZZnONr can be controlled with

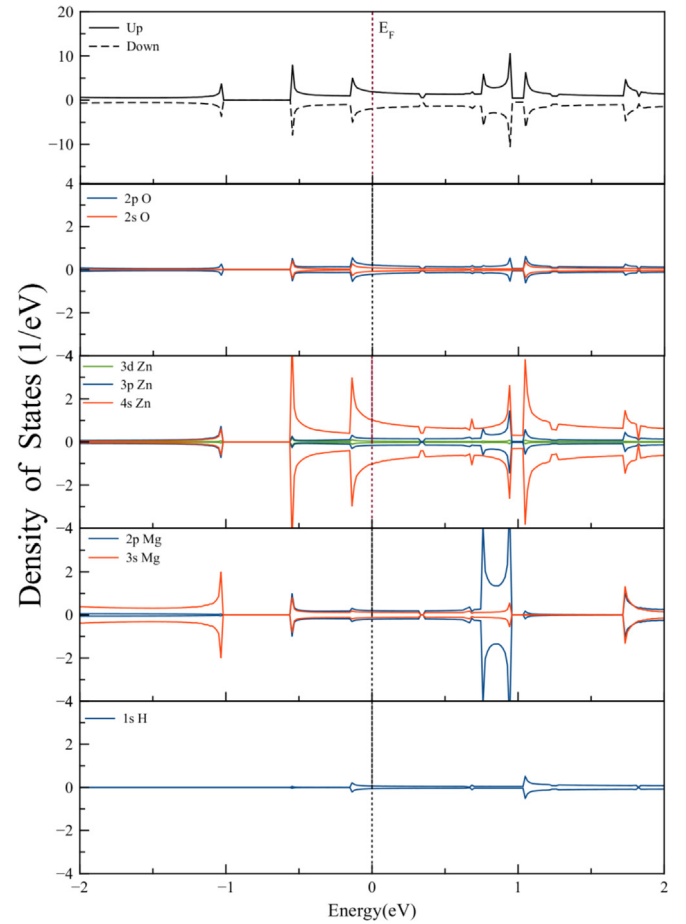


Fig. 7. Total DOS and PDOS of ZZnONr passivated with Mg for Zn-rich edge.

Table 1

Calculated electronic parameters for ZZnONrs passivated with Mg and H atoms.

#ZZnONr	Formation Energy (eV)	Type of bandgap	E_{gap} (eV)
Bare	–	–	0
Both edge H	–	Direct	0.460
Both edge Mg	3.39	Direct	0.006
Zn-rich edge Mg	–3.38	–	0
O-rich edge Mg	102	–	0

width of nanoribbons. Previously, ZZnONrs have been shown the increasing of spin properties depending on increasing of nanoribbon's width [9]. Furthermore, as seen in Fig. 2 for 12 atom width of ZZnONr, the electronic band gap is closed. The electronic band structure and DOS for 10-ZZnONr passivated with H are plotted in Fig. 3. The blue and red lines are represented spin up and spin down band structures, respectively. It is shown that the calculated 10-ZZnONr has a direct bandgap semiconductor behavior. The spin down band gap and spin up band gap values are found to be 0.047 and 0.095 eV, respectively. Because 10-ZZnONr is the depending on spin properties, it has been investigated more details on the electronic properties of ZZnONr passivated with Mg for both edges of the structure.

The electronic band structures of ZZnONr passivated with Mg atoms which have the different ribbon widths are shown in Fig. 4. The electronic band gap is narrower and then closed as increases the width of ZZnONr from 4 to 10 atom width. Similar to ZZnONr passivated with H, ZZnONrs passivated with Mg have exhibited a similar closing band gap trend as increases the nanoribbon's width. This behavior is expected as shown in previous nanoribbon studies [42]. It is shown that all investigated electronic band structures have a nearly direct band gap. As

increase width of nanoribbon, the band structures become to show a linear dispersion, unlike conventional parabolic electronic band structure. Also, it is clearly shown that the electronic band structure of ZZnONr passivated with Mg atoms had 8 and 10 atom width have a band structures graphene-like. Moreover, all studied structures have not been exhibited spin-dependent properties. Contrary to GNRs, the edges of ZnO nanoribbons are different from each other as one edge is an O-rich edge, other edge is a Zn-rich edge. Therefore, the electronic properties of ZZnONrs are strongly dependent on the edges of ZZnONrs.

Additionally, to determine the effect of Mg passivation for O-rich and Zn-rich edges on electronic properties 10-ZZnONr, the electronic band structure of ZZnONrs passivated with Mg atoms for only one edge have been calculated and are shown in Fig. 5. As it can be seen from Fig. 5a), the electronic band structure of ZZnONr passivated with Mg for O-rich and Zn-rich edges has a metallic behavior. In addition, unlike ZZnONr passivated with Mg for O-rich edge structure, ZZnONr passivated with Mg for Zn-rich edge has not been a spin-dependent band structure.

In order to explain the shell contribution of Zn, O, Mg and H atoms to the electronic band structure of ZZnONr, total density of states (DOS) and partial DOS (PDOS) calculations have been performed. Fig. 6 shows the spin-dependent total DOS and PDOS of ZZnONr passivated with Mg for O-rich edge while the valence band is mostly coming from the O-2p shell, the conduction band consists of Zn-4s and O-2p shells both spin up and spin down bands. For the spin up bands, there is a strong density at Fermi level due to the crossing of conduction and valence bands shown in band structure. It is shown that this density is mostly originated from the O-2p shell. Furthermore, H-1s and Zn-2p shells have a lower effect on this density. Fig. 7 shows total DOS and PDOS of ZZnONr passivated with Mg for Zn-rich edge. As shown in Fig. 7, the Zn-4s shell is contributed to total DOS at near Fermi level. Mg-2p shell, as well as Zn-4s shell, has a strong effect on the total DOS about at 1eV. In passivation with Mg atoms of O-rich edge, the spin property is originated from O edge of ZZnONr. It is shown that 2p orbital of O atoms is determined the spin properties of ZZnONr. A previous study reveals that while p orbital of O has a strong spin polarization, d orbital of Zn has a weak spin-polarization [32]. Our result shows a good agreement with results of this study. It can be inferred from that to passive the O-rich edge of ZZnONr can be contributed to spin properties of ZZnONr.

E_F values and the band gap of investigated structures are listed in Table 1. As it can realize that the structure passivated with Mg for Zn-rich edge is the most stable structure among passivated structures. In Table 1, a negative formation energy value show that Mg passivation for Zn-rich edge of ZZnONr can be spontaneously formed [43]. Also, the negative formation energy means that investigated structures can be prepared more appropriate in experimental studies [44].

4. Summary

In this study, the electronic properties of ZZnONr have been investigated using first-principles calculations. To explain electronic structures of ZZnONr passivated with H and Mg atoms, the electronic band structures, total and PDOS and the E_b for each investigated structure have been calculated. It is shown that the increasing widths of ZZnONrs have led to a decrement in energy band gap of the structures. While ZZnONr passivated with Mg for Zn-rich edge have not been shown spin dependency, the structure passivated with Mg for O-rich edge have exhibited spin-dependent band structure. O-rich edge of ZZnONr has a stronger spin polarized structure. The most stable structures have been determined as the largest width ZZnONr passivated with Mg for Zn-rich edge. ZZnONr passivated with Mg atoms for both edges have a graphene-like band structure especially for 8 and 10 atom width structures and this property could be important in terms of electron transport for ZZnONrs. Spin properties of ZZnONr are strongly dependent on edge structures of ZZnONr as Zn-rich and O-rich edges.

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