Ab'initio studies of the structural and electronic properties for single-walled armchair MgONT, SiCNTs and ZnONTs for next generations' optoelectronics

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Abstract

Due to greater demand to use 1D semiconducting chips to replace semiconductors made from bulk structures We studied the structural and electronic properties of free (7, 0) metallic oxides and non-metallic carbide nanotubes. SWMgONT, SWZnONT and SWSiCNT were chosen as the representative model. All the quantum simulation studies were done within DFT *ab'initio* implemented in quantum ESPRESSO. Results obtained for structural properties revealed that the most stable bond lengths of MgONT, ZnONT and SiCNT are 1.80 Å, 1.82 Å and 1.42 Å respectively. The results obtained revealed 2.8 eV band gap for SWMgONT, 0.5 eV for SWZnONT and 0.8 eV for SWSiCNT respectively. Furthermore SWMgONT and SWZnONT are regarded as direct band gap semiconductors while SWSiCNT is regarded as an indirect semiconductor with narrow band gap. The narrow band gap of all the three systems obtained demonstrates their potential in the optoelectronic application in the next generations' sustainability science and technology. Recent studies showed that explorations were conducted on oxide nanotubes such SiO2NT, however to the best of our knowledge, studies of the oxide nanotubes of Mg, Zn and Si have not been reported, hence few literature are available.

How to cite this paper: Itas, Y.S, Suleiman, A.B., Yamusa, A.S., Razali, R. and Danmadami, A.M. (2022). *Ab'initio* studies of the structural and electronic properties for single-walled armchair MgONT, SiCNTs and ZnONTs for next generations' optoelectronics. *Gadau J Pure Alli Sci, 1(2): 160-165.* https://doi.org/10.54117/gjpas.v1i2.42.

1.0 Introduction

Recent advances in the field of sustainability science and technology have revealed the need for greater exploration to behaviors of metallic and nonmetallic nano structures especially nanotube materials (Meenakshi *et al*., 2021). This has become necessary because of greater demand to replace semiconductors made from bulk structures because nano materials make good applicant to smart engineering technology (Hieu *et al.*, 2016). There is high expectations that nanotubes are good candidates for high energy storages, smart optoelectronics, spintronics, smart sensors, and more. For example carbon nanotubes have been used as smart materials for high reflecting surfaces, boron nitride nanotubes has been used as hybrid nanotube to open band gap in graphene formed carbon nanotubes (Vyom *et al.*, 2015), other non-metallic oxide nanotubes were also used in different fields of material science and engineering, for example effects of SO2 adsorption were studied on MgO surface both theoretically and experimentally (Honghong *et al.*, 2020) ..

Best on the available exploration of the literature, studies of magnesium oxide nanotubes were very few.

Therefore there is need to explore more about this nanotube across different chirality. Magnesium oxide nanotubes (MgONTs) are types of nanotubes obtained by rolling 2D sheet of MgOthis nanotube served as an efficient catalyst and has been the focus of considerable attention because it catalyzes a variety of organic reactions, such as aldol reaction, synthesis of chiral epoxy ketones and chiral nitro alcohols (Muruga *et al.*, 2012). It is one of the metallic oxide nanotube, it can exist as armchair, zigzag or chiral depending on the orientation of rolling the hexagonal magnesium oxide mono sheet. Another type of metal oxide nanotube is Zinc oxide nanotube, just as the case of MgONT, it is prepared when hexagonal mono sheet of ZnO is rolled to form a cylindrical nanotube. This research will try to explore the electronic properties of metallic and nonmetallic oxide nanotubes by taking MgONT, ZnONT and SiO$_2$NT as a representative samples. Recent studies showed that explorations were conducted on oxide nanotubes such SiO2NT (Ogihara, 2016), however to the best of our knowledge, studies of the oxide nanotubes of Mg, Zn and Si have not been reported, hence few literature are available.

2.0 Materials and methods
The microscopic structure of zigzag (7, 0) SWMgONT, SWZnONT and SWSiCNT is closely related to that of zigzag SWCNT (Yuqing *et al.*, 2019), therefore the tubes are usually levelled in terms of the graphene hexagonal lattice vectors. Furthermore, comparing structure of all the systems to graphene lattice gives room for theoretical derivation of many properties of the materials under study. The structures of the CNTs are described in terms of the chirality of the tube otherwise helicity. This is defined by the chiral vector C_h and the chiral angle θ, the chiral vector can be described in terms of the lattice translational indices (n, m) and the unit vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. Structural optimizations of all systems were done by considering the lattice parameters of each atom, bond length and chiral angles were also considered. The zigzag SWMgONT, SWZnONT and SWSiCNT were all considered to be of (7, 0) configurations. The calculated chirality were obtained by implementing the equation

$$C_h = na_1 + ma_2 \qquad (1)$$

Where *m* and *n* are the integers which denote the number of steps of the zigzag Mg-O, Zn-O and Si-C bonds along the hexagonal lattice. The degree of twisting the tube is determined by the chiral angle θ between C_h and a_1 (Chang *et al.*, 2007).

The structural and electronic responses of the system of (7, 0) SWMgONT, SWZnONT and SWSiCNT were computed using the DFT *ab'initio* as implemented in quantum ESPRESSO (Maigari *et al.*, 2022) (Sushant *et al.*, 2018). The maximum number of atoms in each case is 28. The nanotubes were built by

rolling up a considerably relaxed 2D sheets of MgO, ZnO and SiC respectively. The oxygen atom protrudes from the Mg, Zn and Si planes in an alternate direction by 0.38 Å. The nanotube bond length was ensured to be 1.82 Å, 1.80 and 1.52 for MgO, ZnO and SiC respectively. Kohn-Sham equations were applied by implementing the DFT *ab'initio* quantum computing (Chien *et al.*, 2021) framework within the Perdiew-Burke-Emzahope (PBE) exchange functional. The energy cut-off value for the construction of the plane-wave basis was achieved at 60 Ry, and the k-point value which correlates to the ecut value was 1 x 1 x 40 k-mesh. This gives a total of 40 nk-points in the first Brillouin zone (BZ). The norm-conserving pseudo potentials were used to calculate the ion-electrons attractive interactions. The maximum force, stress, and displacements were set at 0.06 eV/Å, 0.06 GPa, and 6 x 10^{-4} Å, respectively. The unit cell volume is 5515.67Å^3 with lattice parameters a = 16.68 Å and c = 7.68 Å.

3.0 Results and discussion
3.1 Structural properties
The optimal and equilibrium structure of the model (7, 0) SWMgONT, SWZnONT and SWSiCNT were studied, the results were outlined in Figure 1. All the structures were optimized by rolling 2D monolayers of their corresponding MgO, ZnO and SiC respectively. The materials were highly stable by ensuring that he bond length of MgO were ensured at 1.80 Å, a 1.82 Å bond length was also ensured for ZnO while 1.42 bond length was ensured for SiC. Therefore, it can be reported that the bond lengths of metallic oxide nanotubes is greater than the bond length of organic oxide nanotubes. Consequently, the Mg-O bond length is found to be the unique quantity to calculate percentage errors in the present study. It has been noted that the MgONT chirality demonstrates significant effects on the bond length, the direction of the bond length along the nanotubes axis is different from their direction along the tube circumference. The results of the structural properties of all the three systems revealed that the bond lengths decrease with diameter.

3.2 Electronic properties
In order to understand well about the physical characteristics of these three nanotubes, there is need to have better explanations about their electronic interactions between energy states, relationships between the HOMO and LUMO and the amount of charge carriers per energy state. Electronic properties are those parameters which fully demonstrates the state and electronic behavior in the material (Itas *et al.*, 2022). In terms of nanotubes, band structure calculations determine the behavior of nanotubes in terms of their energy (E) and momentum (k) (Itas *et al.*, 2020).
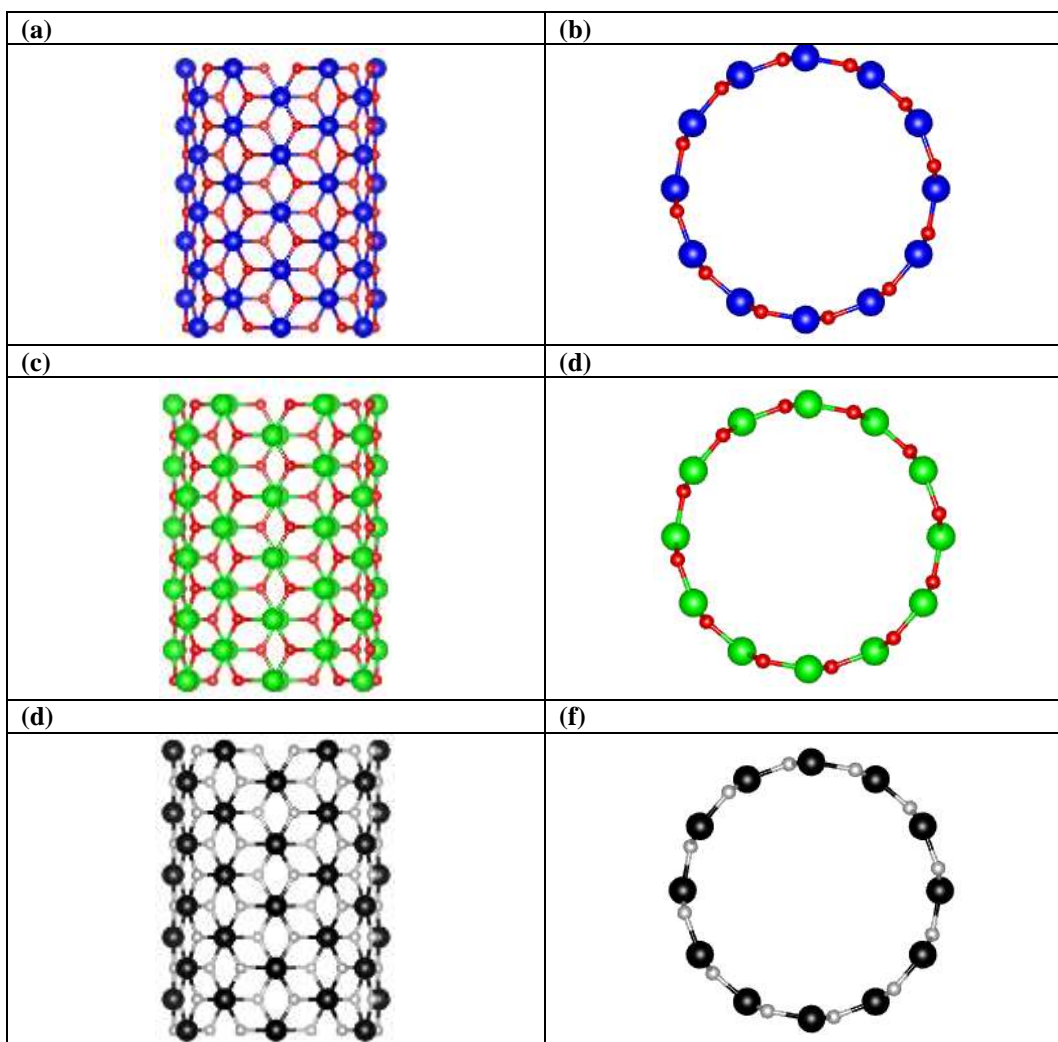
Figure 1. Structural representations of (a) SWMgONT, (b) SWZnONT and (c) SWSiCNT. The blue balls represent mg atom, red balls represent O atom. The Zn atoms are represented by the green balls while the black balls represented C atom.

These are strongly coupled with quantities such as electrical conductivity and dielectric response. This section explains the electronic behaviors of SWMgONT, SWZnONT and SWSICNT materials for applications to sustainability science and technology. The electronic bands structure and DOS for SWMgONT were presented in Figure 2. As can be seen in Figure 2 (a), there were empty band in conduction band up to 1.8 eV, similarly zero bands were seen in the conduction band from -1.7 up to Fermi level, there were no cross bands at the Fermi level and no any intersection at the Dirac point. This region is called the empty states for SWMgONT, as such it is regarded as the band gap. The band gap created as a result of electronic behavior of MgONT is 2.8 eV. This value agreed well with the range of bands obtained for MgONT and other nanotubes (Badar *et al*., 2012). The band gap obtained is a direct band gap

because of amplitude correlation between HOMO-LUMO (Itas *et al*., 2022), on the other hand they are at the same momentum. The narrow band gap of SWMgONT reported in this work reveals it potential in the next generation's optoelectronic applications (Itas *et al*., 2022). To further confirm the reported band structure for SWMgONT, electronic density of states were studied. The result is presented in Figure 2 (b). There is higher intensity of electronic states in the conduction band than in the valence band. Presence of electronic states in the conduction bands is because of presence of delocalized electrons which are highly mobile and are responsible for electrical conductivity in SWMgONT. To justify the band gap obtained, empty electronic states can be seen from -1.8 up 1.8 eV.
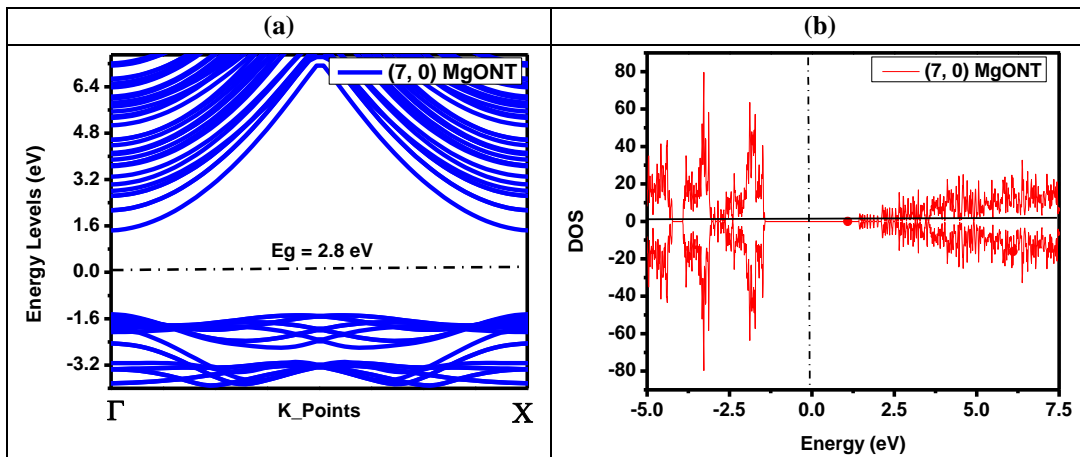
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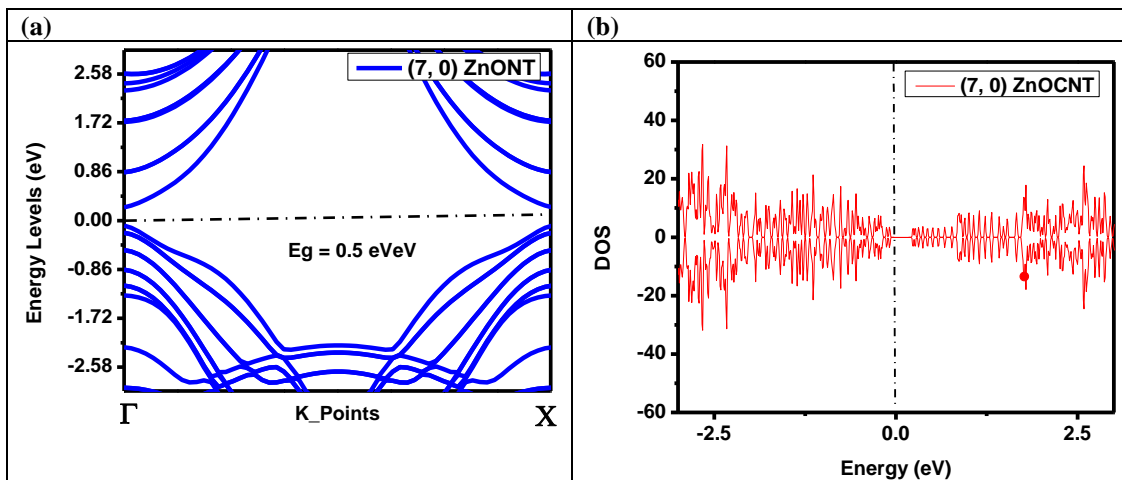Figure 2. Electronic bands and DOS for (7, 0) SWMgONT

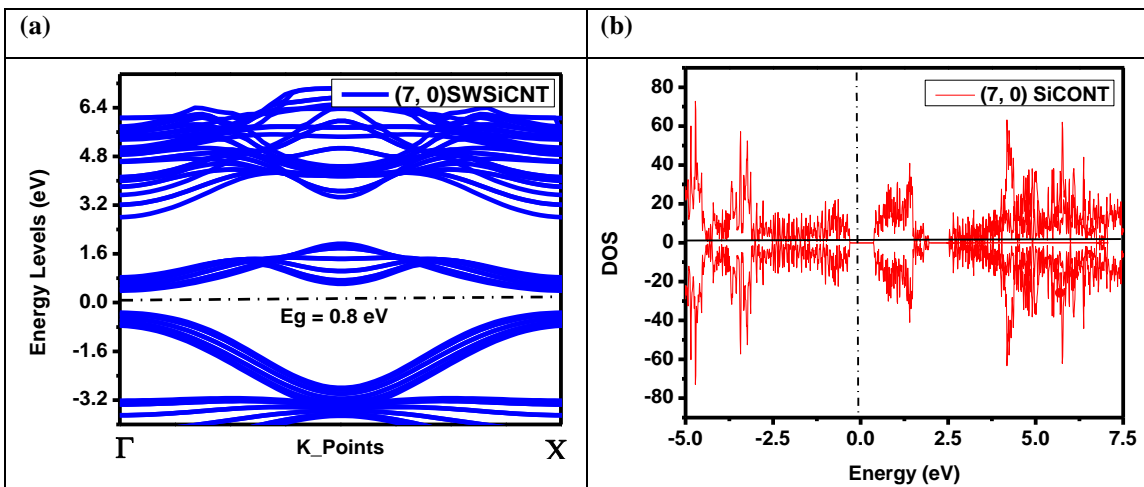Figure 3. Electronic bands and DOS for (7, 0) SWZnONT

Figure 4. Electronic bands and DOS for (7, 0) SWSiCONT

In the case of (7, 0) ZnONT, a very narrow band gap of 0.5 eV was realized (Figure 3(a)), just like SWMgONT, it is also a direct band gap. The band gap of SWZnONT is narrower than SWMgONT because Zn is more electron negative than Mg. The 0.5 band gap of ZnONT demonstrates its candidacy for thermoelectric device fabrication, it also revealed ZnONT as having a high potential for efficient power generation and cooling. The DOS spectrum of Figure 3 (a) show the highest electronic state at 31, therefore it can be stated that there are more energy states in SWMgONT than SWZnONT. Unlike SWMgONT, farely equal states can be seen between conduction band and the valence band.The electronic bands structure for (7, 0) SWSiCNT showed entirely different shape with those of SWMgONT and SWZnONT, this is enough to explain that bands for metallic oxide nanotubes are not the same with bands of organic nanotubes. As shown in Figure 4 (a), an indirect band of 0.8 eV has been obtained for SWSiCNT, the bands are called indirect because the amplitude of HOMO are not at the same momentum with the amplitude of LUMO. Another reason for this is the carbon ability to form covalent bonding with a non-carbon compound. Furthermore, bands gaps for SiCNT decreases with chirality because it is indirect. It has also been esterblished that zigzag SiCNT with n = 5 and 6 are metallic while zigzag SiCNT with n = 7-9 are semiconductors (Larina *et al.*, 2008), our 0.8 eV result for this (7, 0) SWSiCNT confirms this claim. In the DOS spectrum of SWSiCNT shown in Figure 4 (b), two sub bands can be seen in the valence band, these are called intra-bands. This intra–bands transition are as a result of excitations of carbon electrons from one band to another band in the same valence band.

4.0 Conclusion

In this study, the structural and electronic properties of metallic oxides nanotubes and organic nanotubes were studied within DFT *ab'initio* approach. Structural properties revealed the most stable form of SWMgONT, SWZnONT and SWSiCNT are those with bond lengths of 1.80 Å, 1.82 Å and 1.42 Å respectively. Base on this results, the three systems studied can be regarded as good candidates for high elastic moduli applications such as automobiles shock springs. In terms of the electronic properties, it can be reported that zigzag form of metallic oxide nanotubes are semi conducting from n = 7-9, in the case of SiCNT, the results showed that is it semiconducting irrespective of chirality. The electronic bands structure and DOS for SWMgONT obtained revealed that there were empty band in conduction band up to 1.8 eV, similarly zero bands were seen in the conduction band from -1.7 up to Fermi level, there were no cross bands

at the Fermi level and no any intersection at the Dirac point. This region is called the empty states for SWMgONT, as such it is regarded as the band gap. The band gap created as a result of electronic behavior of MgONT is 2.8 eV. This value agreed well with the range of bands obtained for MgONT and other nanotubes.

List of abbreviations

MgONT = Magnesium Oxide Nanotube
SiCNTs = Silicon Carbide Nanotubes
SWMgONT = Single Walled Magnesium Oxide Nanotubes
ZnONTs = Zinc Oxide Nanotubes

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