Materials Research. 2016; 19(3): 497-504
DOI:http://dx.doi.org/10.1590/1980-5373-MR-2015-0432

Energetic and electronic properties in a multilayered ZnO graphene-like nanostructure

Flaviano Williams Fernandes[a]*, Vitor Fernando Gigante de Paiva[a], Gilmar Patrocínio Thim[a]

[a]Departamento de Física, Instituto Tecnológico de Aeronáutica, São José dos Campos, 12228-900, São Paulo, Brazil

Received: July 28, 2015; Revised: October 15, 2015; Accepted: December 16, 2015

Nanostructures based on ZnO have been widely studied due to their electronic and piezoelectric properties. Experimental studies have shown that thin films based on ZnO can be used as chemical and optoelectronic sensors. The great goal of this work is to study of the role of the number of graphene-like layers in the physical properties of the ZnO. Therefore, the geometrical and electronic properties of graphene-like structures will be compared with the wurtzite one. In this work, the pn-type semiconducting behavior of the graphene-like structures and its relationship with the number of layers will be also analyzed.

Keywords: *First principle calculation, Graphene structure, ZnO nanostructure*

1 Introduction

Crystalline ZnO is a semiconductor with wide GAP and has an excellent piezoelectric property. These features suggest a great application for ZnO as transistors, gas sensors and optoelectronic devices, among others. Different ZnO nanostructures studied by theoretical and experimental techniques. Therefore, ZnO nanostructures have attracted great interest of researchers and engineers because of their excellent physical properties with enormous potential in technology. For example, nanowires [1-9] were synthesized in laboratories for optoelectronic sensors and Zhou et al., observed by density functional theory, that ZnO nanowires act as excellent chemical sensors [7,8,10-12]. In special, theoretical studies [13-15] showed that thin films of ZnO combined with carbon nanotubes have interesting physical properties, such as weightlessness, elasticity and piezoelectricity. These properties suggest great applications in aerospace design and sensor development for detecting fractures or/and defects in the structure. However, few theoretical studies have been made so far in order to analyze two-dimensional structures of ZnO. For instance, Tu, Hu [13] observed interesting physical properties of the two-dimensional structure of ZnO and their results were compared to the carbon nanostructure. However, the analysis proposed by him is limited by only one graphene layer.

In this paper a theoretical study was performed to investigate the effect of the graphene layers number on ZnO graphene-like structure and the results were compared to the wurtzite structure values. Therefore, three different systems composed by two-dimensional ZnO were used to get the graphene-like structures, and they were studied by density functional theory and periodic boundary conditions. The results showed that ZnO thin films have a flat honeycomb structure similar to graphene, which the value of Zn-O bond length in ZnO graphene form is greater than that in wurtzite form and Zn-O bond length decreased with the increase in the layer number. Furthermore, the n-type behavior of ZnO graphene-like depends on the number of graphene layers.

*e-mail: flaviano@ita.br

2 Computational procedure

Density functional theory (DFT) was made using the projector augmented-wave function data set proposed by Kresse [16] and the generalized gradient approximation (GGA) by Perdew et al., [17]. Abinit software [18] was used to perform the DFT calculation with periodic boundary conditions. The convergence of the wave functions was obtained after the error in the energy reaches 10^{-6}Hartree. The energy cut-off for the plane wave basis was set to 24 Hartrees and the plane wave density grid to 60 Hartrees. The Monkhorst-Pack method[19] shifted at the Γ point was used to perform the K-point distribution in the first Brillouin zone and grid meshes of 6x6x5 and 8x8x1 were used for wurtzite and graphene-like structures. The zinc-oxygen charge transfer values were based on the Hirshfeld method [20].

Broyden-Fletcher-Goldfarb-Shanno minimization [21] was used to optimize the atomic coordinates and the unit cells of wurtzite and graphene-like structures. All atoms were allowed to relax until the forces were smaller than $5x10^{-4}$Hartree/Bohr for wurtzite and for graphene-like structures. Various modifications were made in the wurtzite cell in order to construct a ZnO two-dimensional structure: The wurtzite unitary cell was replicated along the three directions. The highest and lowest atoms were removed from the replicated cell. Next, the unitary cell parameters were adjusted and the atomic coordinates were optimized in order to obtain the two-dimensional most stable structure of the graphene-like. A vacuum distance of least 10 Å was performed to avoid interactions between adjacent images. Fig. 1 shows the geometries of wurtzite (a) and graphene-like structures (b, c and d) after optimization.

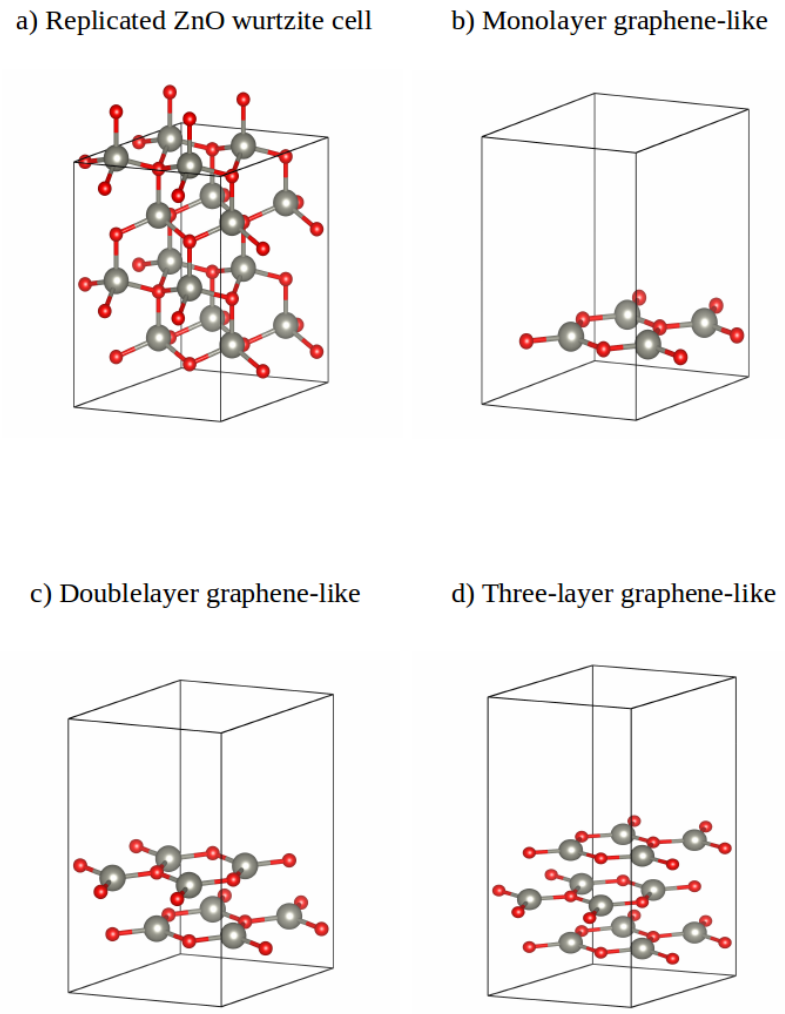

Figure 1: Replicated wurtzite structure along the xyz directions (a) and two-dimensional ZnO graphene-like structures (b, c and d). The geometries were obtained after optimization.

3 Results and discussion

The most stable ZnO bulk structure is the wurtzite lattice [11, 14, 23, 25]. According to Karzel et al., [22] the crystal lattice parameters of wurtzite (a, b, c) are a = b = 3.25 Å and c = 5.204 Å whereas the internal parameter u (u = c/a) corresponds to 1.602. Table 1 presents some wurtzite lattice parameters theoretically (in this work and in others papers [14,23-25] and experimentally determined [22]. In this work, the crystal lattice parameters for wurtzite are a = 3.197Å, c = 5.179 Å and u = 1.62, which are in good agreement with the experimental data proposed by Karzel et al., [22] with errors less than 2%. Table 1 also shows the crystal lattice parameters of ZnO graphene-like structures after optimization and theoretical and experimental results found in literature. The parameter a was 3.286 Å for the monolayer graphene-like structure, which is higher than that of wurtzite one.

Fig. 1 shows the structures of wurtzite (Fig.A) and graphene like ZnO of one layer (Fig.B), two layers (Fig. C) and three layers (Fig.D). These structures were obtained after optimization of the initial cell. Figures 1B, C and D show that the optimized structures are flat and they are similar to the graphene shape. According to Claeyssens et al., [26], ZnO thin films containing less than 18 layers have not the structure of wurtzite, but all layers have structures similar to the graphene. However, Tu [27] estimated that for a unitary cell made by three layers of ZnO graphene-like, the interaction between these layers should be sufficient to deform the structure, there by forming the structure of wurtzite.

Tab. 1 shows the average of the Zn-O bond length of wurtzite and Zn-O graphene-like structures (d_{Zn-O}) obtained in this work and in literature. Karzel et al., [22] obtained the Zn-O bond length of 1.99 Å for wurtzite, while theoretical works [24] found 2.001 and 2.007 Å. However, the values determined by Chai et al., [23] and Pandey et al., [24] using isolated clusters are ranged from 1.817 to 1.930 Å, which are shorter than wurtzite ones. Furthermore, Tu, Hu [13] found 1.852 Å for monolayer structure of ZnO using DFT method while Topsakal et al., [25] found 1.895 Å. In this work, the Zn-O bond length was 1.897 Å for monolayer graphene-like

structure and the values found for two and three-layers were larger than 2 Å. Therefore, the Zn-O bond length depends on the number of graphene layers in the graphene-like structure, due to the increasing of the binding energy between neighboring atoms.

Tab. 2 shows the Zn-O bond length (d^{bl}) between neighboring atoms of the same graphene layer in a ZnO graphene-like structure. The values for the Zn-O bond length in the mono, double and three-layer graphene-like structures are 1.897, 1903 and 1.903 Å, respectively, which are smaller than that one found for the wurtzite structure (1.954 Å). These results are in agreement with those reported by Tu (1.852 Å) [14,27]. Tab. 2 also shows the interlayer distance between adjacent layers (d^{al}), which was determined by the average distance between zinc and oxygen on different layers (at this point it is important to note that zinc and oxygen, which are on different layers are in the same point in the xy plane). The interlayer distance between adjacent layers for double and three layers were 2.458Å and 2.502 Å, respectively. Tab. 2 also shows the Zn-O bond length parallel to c-axis (d_w^{al}) and the average of three others Zn-O bond lengths (d_w^{bl}) in the wurtzite structure. The values for d_w^{bl} and d_w^{al} were 1.954 and 1.949Å, respectively. In both cases, double and three-layer structures, d^{al} were larger than the Zn-O bond length in the wurtzite structure. Thus, the graphene-like structures reveal that the distance between zinc and oxygen on the same layer is smaller than the ones founded on the different layers.

The interlayer distance between adjacent layers (d^{al}) of the double layer grafene-like structure agrees with values determined by Topsakal (2.314 Å) using x-ray diffraction analysis. However, Lebegue et al., [29] found the value of 3.33 Å in a multilayer graphene with ABAB stacking sequence, giving the interlayer distance of ZnO graphene-like structures a smaller value compared to carbon graphene. Therefore, a smaller d^{al} permits that ZnO graphene-like structures get a smaller vacuum distance compared to carbon graphene.

Figs. 2-4 show the band structures calculated for the three structures of ZnO graphene-like after optimization. The red dashed line is the Fermi level found for wurtzite, where the GAP is 0.79 eV, whereas the experimental value is 3.4 eV [28]. This underestimation is due to some approximations of the electronic correlation effects at sub-level d, which is caused by the GGA functional. Despite that, it is possible to see an evident decrease of the GAP with the number of graphene layers. By the way, ZnO graphene-like showed larger GAPs than wurtzite. According to the GAP values, all structures of ZnO graphene-like are semiconductors with a direct GAP at the Γ point. The monolayer structure showed a GAP of 1.61 eV which is in a good agreement with the results found by Tu [27] without GW correction (1.762 eV). The GAP for the double layer and three-layer structures was 1.34 eV and 1.22 eV, respectively. Fig. 5 shows the GAP related to the number of graphene layers. It is possible to see that the number of graphene layers tends to decrease the value of the GAP.

Figs. 2 to 4 also show the density of states (DOS) for ZnO graphene-like on different graphene-like layers. The DOS values of ZnO graphene-like has only one graphene-like layer suddenly decay near the Fermi level when it is

Table 1: Crystal lattice parameters and structure found in this work and theoretical and experimental values for wurtzite and graphene-like structures in literature.

Reference	Structure	d_{Zn-O}(Å)	a (Å)	c (Å)	c/a
This work	Monolayer	1.897	3.286	∞	∞
	Two-layer	2.088	3.295	∞	∞
	Three-layer	2.017	3.295	∞	∞
	Wurtzite	1.949	3.197	5.179	1.620
Literature	Isolated cluster†	1.930	∞	∞	-
	Isolated cluster‡	1.885	∞	∞	-
	Isolated cluster‡	1.817	∞	∞	-
	graphene-like♯	1.895	3.283	∞	∞
	graphene-like^{s}	1.852	3.199	∞	∞
	wurtzite♯	2.001-2.007	3.280	5.300	1.616
	wurtzite^{b}	1.990	3.250	5.204	1.602

† DFT by Pandey et al [24]; ‡ DFT by Chai et al [23]; ♯ DFT by Topsakal et al [25]; ʒ DFT by Tu et al [13]; ♭ Experimental results proposed by Karzel et al [22]

Table 2: Binding energy (E_B), net charge transfer (ΔQ), average energy and their contributions at each sub-level ($E_{s,p,d}$). The Zn-O bond lengths d^{bl} and d^{al}. The unities are eV, elementary charge unity and angstrom.

Structure	Layer	d^{bl}	d^{al}	ΔQ	E_B	Zn			O
						E_s	E_p	E_d	E_p
Graphene-like	1	1.897	∞	0.400	-8.06	-11.02	-6.91	-8.01	-5.60
	2	1.903	2.458	0.376	-8.20	-8.27	-5.72	-6.44	-4.34
	3	1.903	2.502	0.371	-8.23	-7.46	-5.46	-6.05	-3.99
Wurtzite	∞	d_w^{bl}	d_w^{al}	0.323	-8.53	-1.99	-0.64	-0.74	0.70
		1.954	1.949						

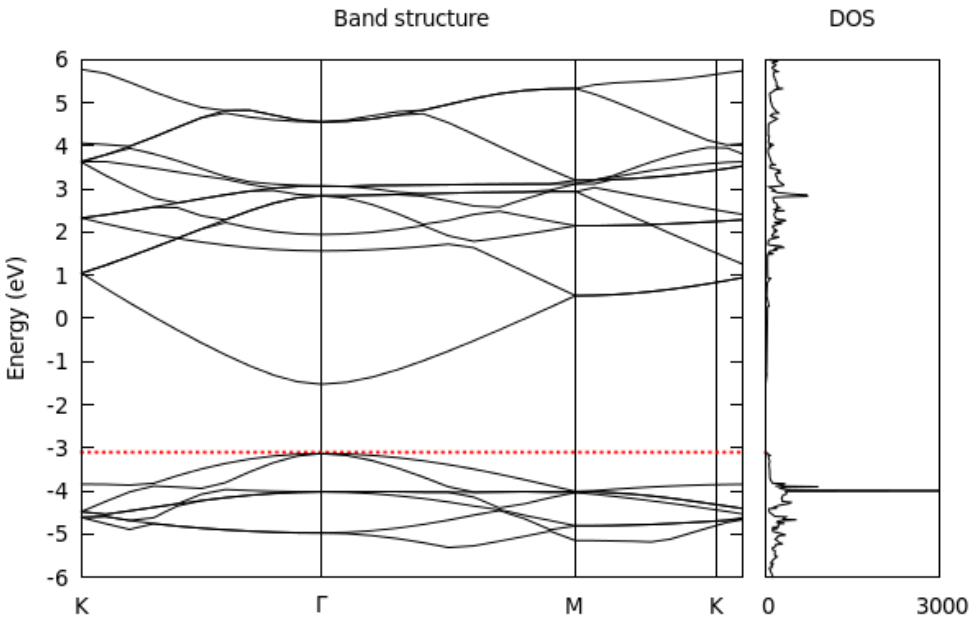

Figure 2: Band structure and DOS of ZnO in the monolayer graphene-like structure. The red dashed line is the Fermi level found for wurtzite.

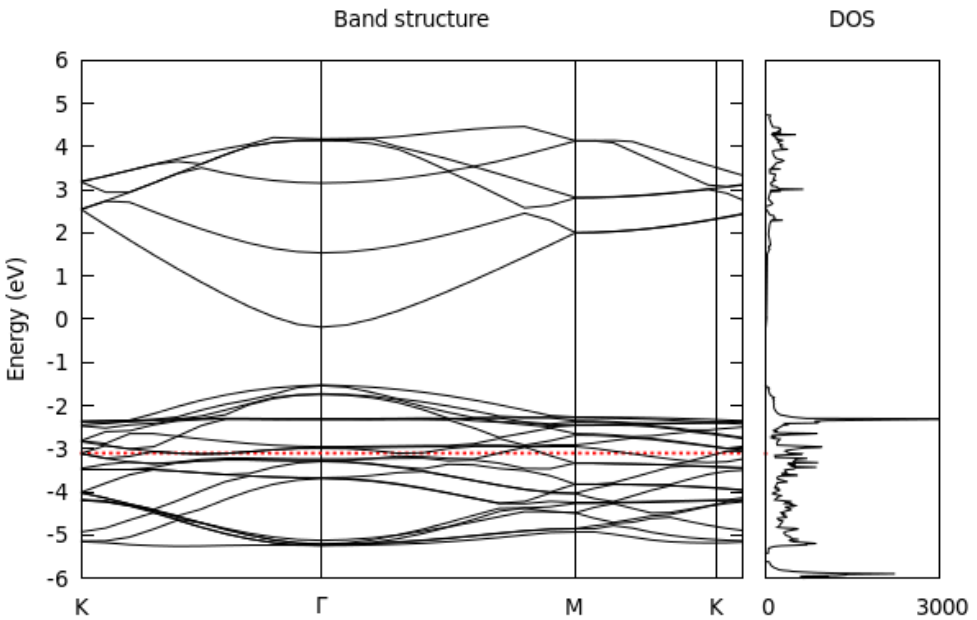

Figure 3: Band structure and DOS of ZnO in the doublelayer graphene-like structure. The red dashed line is the Fermi level found for wurtzite.

compared to the wurtzite one. Moreover, the double and three graphene-like layers showed a more intense peak in the DOS (at -2.5 eV) which is associated with a large quantity of degenerated states. A meaningful increase in the band levels and the density of states under the valence band can be noted in Figures 2-4 for structures using double and three graphene-like layers. Furthermore, the energies of the band levels under the HOMO state also increase compared to the Fermi level found for wurtzite. Consequently, a shift of the Fermi level of the graphene-like structures towards the conduction band of the wurtzite can be observed. Thus, the graphene-like structure becomes an n-type semiconductor for a larger number of graphene-like layers. A suddenly decay in the DOS, going from the highest occupied level (HOMO) returning to the lowest occupied level (LUMO) was observed. Thus, the monolayer graphene-like presents

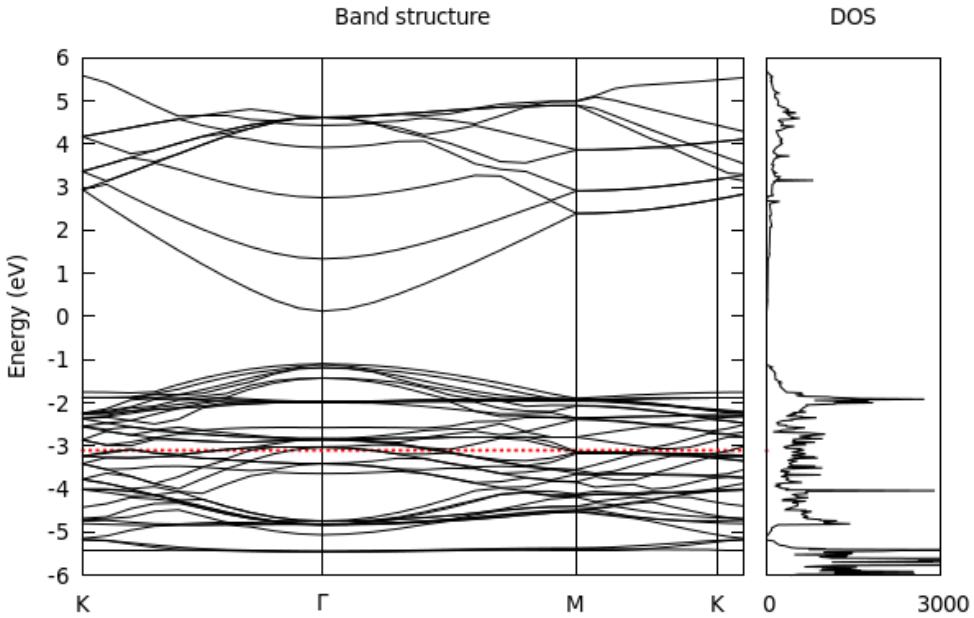

Figure 4: Band structure and DOS of ZnO in the three-layer graphene-like structure. The red dashed line is the Fermi level found for wurtzite.

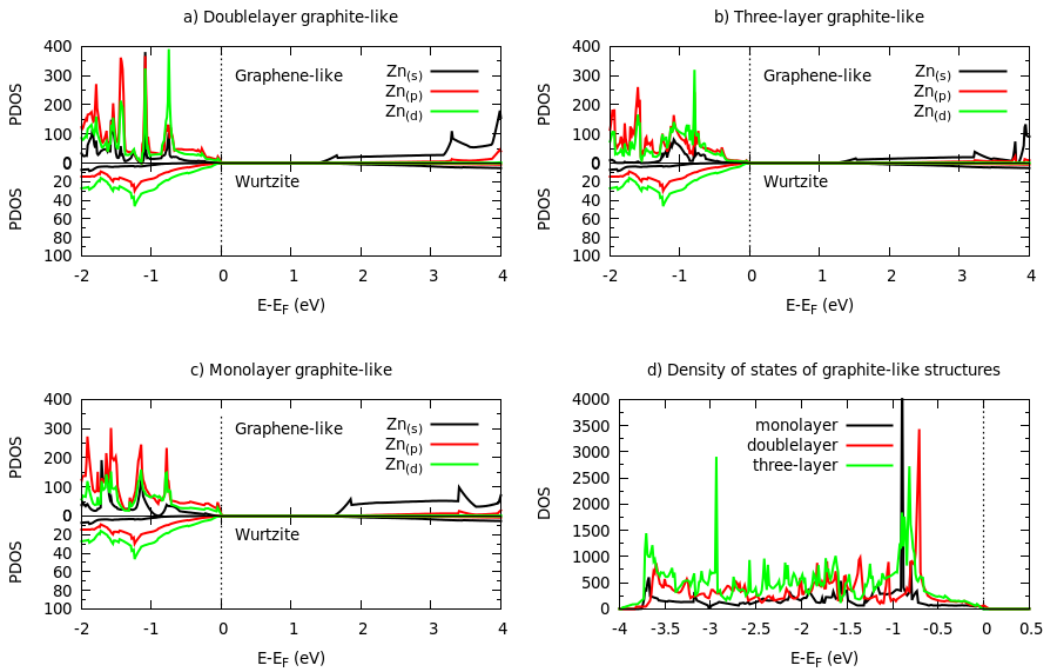

Figure 5: PDOS of the zinc within the structure of graphene-like forms (top-half) and wurtzite (lower-half). The black, red and green lines represent the sublevels. The DOS of graphene-like structures is shown below on the right.

a well-defined region of band GAP, but the wurtzite does not, where a slightly soft decay is observed at sub-levels of the zinc in the conduction band near the LUMO state. Therefore, the wurtzite shows a lower value for the GAP compared to ZnO graphene-like structure.

The increase in the number of graphene-like layers increases the quantity of energy level which raises the density of states (DOS). Therefore, the consequence is that the valence band energy becomes higher than the Fermi level of the monolayer case. Consequently, the GAP decreases with the increase in the number of the graphene-like layers. The Fermi level found for the monolayer graphene-like structure is 3.13 eV while for wurtzite is 3.9 eV. However, the Fermi level increases for a large number of Zn-O

graphene-like layers (-3.11 eV for monolayer, 1.54 ev for double layer and -1.12 eV for three-layer cases). Therefore, the ZnO graphene-like becomes an n-type semiconductor when $N >> 1$ (N represents the number of graphene layers). This behavior agrees with the electrical conductivity analysis of ZnO thin films proposed by Caglar et al [12].

The partial density of states (PDOS) of the sub-levels s, p and dare presented for zinc and oxygen in Figs. 5 and 6, respectively. PDOS was calculated for the three different structures of the ZnO graphene-like (top-half of the frames a, b and c in Figs. 5 and 6) and the results were compared to wurtzite (lower-half of the frames a, b and c in Figs. 5 and 6). In the valence band, the comparison between the PDOS of the zinc and oxygen indicates that DOS of the ZnO graphene-like is mainly filled by the sub-level p of the oxygen. Moreover, both structures (graphene-like and wurtzite) have the sub-level p predominantly filled with the energy states of oxygen. However, zinc is filled with sub-levels s, p and d. The region near the highest occupied state (HOMO) is predominantly filled with the sub-levels p and d of zinc and oxygen in wurtzite, while ZnO graphene-like structure is almost homogeneous among these three sub-levels.

The average energy of the sub-levels s, p and d was determined by Eq. 1,

$$E_l = \frac{\int_{-\infty}^{E_F} \varepsilon \eta_l(\varepsilon) d\varepsilon}{\int_{-\infty}^{E_F} \eta_l(\varepsilon) d\varepsilon}, \quad (1)$$

where η_l represents the partial density of states of sub-level l ($l = s, p, d$) under the Fermi level. The values for the average energy of each level are also showed in Tab. 2. These energies are important because they describe the contribution of these levels to electronic process (more negative means more active to electronic process), such as hybridization and electronic transport [30]. In the wurtzite and graphene-like structures, the E_l value found for the oxygen is 0.7 eV, therefore it does not contribute actively in the hybridization instead of the sub-level s of the zinc which is the most active one (-11.02 eV). The value of the average energy of the sub-levels s, p and d gradually increases as the number of graphene-likelayers increases. Therefore, due to the bidimensional confinement of electrons, the sub-levels of atoms that compose the graphene-like layers tend to be most active to electronic process when the number of graphene-like layers decreases.

The stability of the Zn-O bond energy was analyzed by the binding energy in the wurtzite and graphene-like structures according to the following formula:

$$E_B = E_{ZnO} n^{-1} - (E_{Zn} + E_O), \quad (2)$$

where n is the number of bonds between zinc and oxygen atoms. $E_{Zn,O}$ represents the total energy of zinc and oxygen atoms and E_{ZnO} is the energy of ZnO composed by 2n atoms. The binding energy of wurtzite was -8.53 eV, which is in a good agreement with the results proposed by Tu et al., [13] (-8.95 eV). Fig. 7 also shows the binding energy as a function of the number of graphene layers. However, the Zn-O binding energy for monolayer graphene-like (8.06 eV) is higher than wurtzite, revealing that Zn-O bond of the graphene-like structure is less stable. Furthermore, Tab. 2 shows that the binding energy tends to decrease as the number of graphene layer increases, where for the double layer E_B is -8.2 eV while the three-layer case is 8.23 eV.

Tab. 2 also shows the absolute value average of the net charge of zinc and oxygen atoms (ΔQ). The net charge

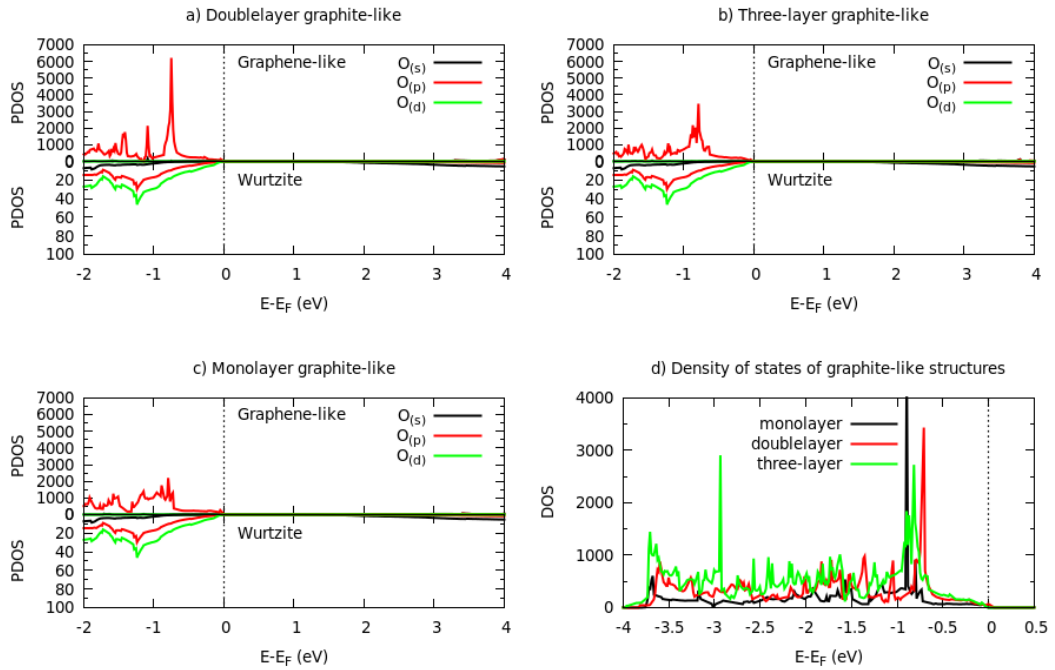

Figure 6: PDOS of the oxygen within the structure of graphene-like forms (top-half) and wurtzite (lower-half). The black, red and green lines represent the sublevels. The DOS of graphene-like structures is shown below on the right.

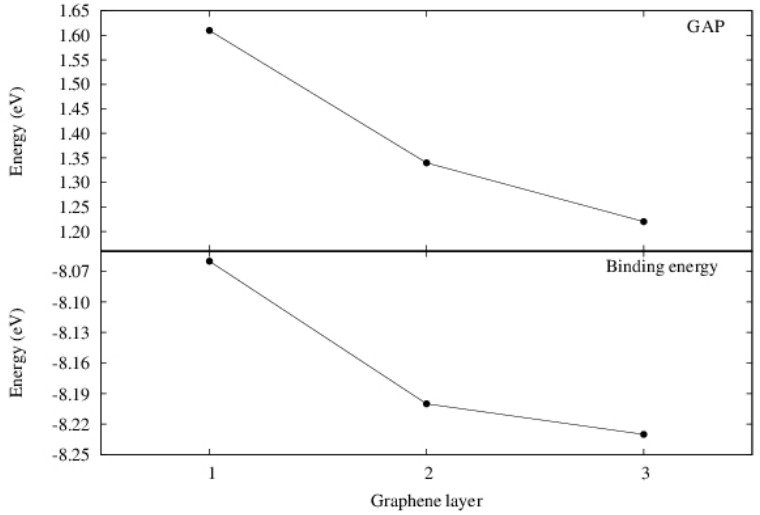

Figure 7: GAP and binding energies of graphene-like structures composed by different numbers of graphene layers.

per atom in the graphene-like structure (mono, double and three-layer)is higher than in wurtzite (0.323e). The monolayer structure showed a net charge (ΔQ) of 0.4e, this value is the highest one among the three graphene-like structures (0.376e for double layer and 0.371e for three-layer). Due to Coulomb law, it is expected a more intense electrostatic energy for larger values of ΔQ, as a result, the atomic interaction also increases. However, due to the charge transfer between atoms of different layers, ΔQ gradually decreases when the number of graphene layers increases.

4 Conclusion

The structural and electronic properties of the ZnO graphene-like were obtained and compared with wurtzite using the plane wave expansion and DFT theory. The number of graphene-like layers in the graphene-like structure substantially affects the electronic and structure properties of ZnO. The Zn-O bond length between zinc and oxygen is lower than the ones found in the wurtzite. The GAP of the ZnO graphene-like structure tends to decrease with the number of graphene-like layers, which are larger than those of wurtzite. The analysis of the partial density of states showed that the monolayer graphene-like structure has a great contribution of the p and d sub-levels of zinc near the HOMO state, therefore this contribution tends to decrease with the increase in the number of graphene-like layers. The average of the sub-levels s, p and d of zinc and oxygen tends to increase for a lower number of graphene-like layers. Therefore, the donor-like behavior depends on the number of graphene-like layers, where the ZnO graphene-like becomes an n-type semiconductor. Furthermore, the net charge transfers between zinc and oxygen in graphene-like structures are higher than wurtzite, where the net charge gradually decreases with the number of graphene-like layers.

5 Acknowledgement

The authors thank to CAPES (005/2014) for financial support.

6 References

1. Huang MH, Mao S, Feick H, Yan H, Wu Y, Kind H, et al. Room-temperature ultraviolet nanowire nanolasers. *Science*. 2001;292(5523):1897–1899.
2. Wei A, Pan L, Huang W. Recent progress in the ZnO nanostructure-based sensors. *Materials Science and Engineering: B*. 2011;176(18):1409–1421. doi:10.1016/j.mseb.2011.09.005
3. Wang ZL. ZnO nanowire and nanobelt platform for nanotechnology. *Materials Science and Engineering: R: Reports*. 2009;64(3-4):33–71. doi:10.1016/j.mser.2009.02.001
4. Heo Y, Norton D, Tien L, Kwon Y, Kang B, Ren F, Pearton S, LaRoche J. Zn0 nowire growth and devices. *Materials Science and Engineering: Reports*. 2004;47(1-2):1–47.
5. Cui J. Zinc oxide nanowire. *Materials Characterization*. 2012;64:43–52.
6. Wang ZL. *Materials Today*. 2007;10(5):20–28.
7. Suchea M, Christoulakis S, Moschovis K, Katsarakis N, Kiriakidis G. ZnO transparent thin films for gas sensor applications. *Thin Solid Films*. 2006;515(2):551–554. doi:10.1016/j.tsf.2005.12.295
8. Pearton S, Ren F, Wang YL, Chu B, Chen K, Chang C, et al. Recent advances in wide bandgap semiconductor biological and gas sensors. *Progress in Materials Science*. 2010;55(1):1–59. doi:10.1016/j.pmatsci.2009.08.003
9. Djurišić A, Ng AMC, Chen XY, Djuriić AB, Chen XY. ZnO nanostructures for optoelectronics: material properties and device applications. *Progress in Quantum Electronics*. 2010;34(4):191–259.
10. Zhou Z, Li Y, Liu L, Chen Y, Zhang SB, Chen Z. Size-and surface-dependent stability, electronic properties, and potential as chemical sensors: computational studies on one-dimensional ZnO nanostructures. *The Journal of Physical Chemistry C*. 2008;112(36):13926–13931.
11. Mitra P, Chatterjee A, Maiti H. ZnO thin film sensor. *Materials Letters*. 1998;35(1)33–38. doi:10.1016/S0167-577X(97)00215-2
12. Caglar M, Ilican S, Caglar Y, Yakuphanoglu F. Electrical conductivity and optical properties of ZnO nanostructured thin film. *Applied Surface Science*. 2009;255(8): 4491–4496.

13. Tu Z, Hu X. Elasticity and piezoelectricity of zinc oxide crystals, single layers, and possible single-walled nanotubes. *Physical Review B*. 2006;74(3):035434.
14. Gao F, Zhang L, Huang S. Zinc oxide catalyzed growth of single-walled carbon nanotubes. *Applied Surface Science*. 2010;256:2323–2326.
15. Baibarac M, Baltog I, Lefrant S, Mevellec JY, Husanu MM. Vibrational and photoluminescence properties of composites based on zinc oxide and single-walled carbon nanotubes. *Physica E: Low-dimensional Systems and Nanostructures*. 2008;40(7):2556–2564. doi:10.1016/j.physe.2007.09.034
16. Kresse G. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B*. 1999;59(3):1758–1775.
17. Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. *Physical Review Letters*. 1996;77(18):3865– 3868.
18. Gonze X, Amadon B, Anglade PM, Beuken JM, Bottin F, Boulanger P, et al. *Computer Physics Communications*. 2009;180(12):2582–2615.
19. Monkhorst HJ, Pack JD. Special points for Brillouin-zone integrations. *Physical Review B*. 1976;13(12):5188–5192. DOI: http://dx.doi.org/10.1103/PhysRevB.13.5188
20. Hirshfeld FL. Bonded-atom fragments for describing molecular charge densities. *Theoretica Chimica Acta*. 1977;44(2):129–138. DOI 10.1007/BF00549096
21. Schlegel HB. Optimization of equilibrium geometries and transition structures. *Journal of Computational Chemistry*. 1982;3(2):214–218. DOI: 10.1002/jcc.540030212
22. Karzel H, Potzel W, Köfferlein M, Schiessl W, Steiner M, Hiller U, et al. Lattice dynamics and hyperfine interactions in ZnO and ZnSe at high external pressures. *Physical Review B*. 1996;53(17):11425–11438.
23. Chai GL, Lin CS, Cheng WD. First-principles study of ZnO cluster-decorated carbon nanotubes. *Nanotechnology*. 2011;22(44):445705.
24. Pandey D, Yadav P, Agrawal S, Agrawal B. Structural and electronic properties of ZnO nanoclusters: a B3LYP DFT study. *Advanced Materials Research*. 2013;650:29–33.
25. Topsakal M, Cahangirov S, Bekaroglu E, Ciraci S. First-principles study of zinc oxide honeycomb structures. *Physical Review B - Condensed Matter and Materials Physics*. 2009;80(23):1–15.
26. Claeyssens F, Freeman CL, Allan NL, Sun Y, Ashfold MN, Harding JH. Growth of ZnO thin films—experiment and theory. *Journal of Materials Chemistry* .2005;15(1):139-148.
27. Tu ZC. First-principles study on physical properties of a single ZnO monolayer with graphene-like structure. *Journal of Computation Theoretical Nanoscience*. 2010;7(6):1182-1186.
28. Chichibu SF, Sota T, Cantwell G, Eason DB, Litton CW. Polarized photoreflectance spectra of excitonic polaritons in a ZnO single crystal. *Journal of Applied Physics*. 2003;93:756–758.
29. Lebegue S, Harl J, Gould T, Angyan JG, Kresse G, Dobson JF. Cohesive properties and asymptotics of the dispersion interaction in graphite by the random phase approximation. *Physical Review Letters*. 2010;105(19):1-4.
30. Tang Q, Luo Q. Adsorption of CO2 at ZnO: a surface structure effect from DFT+U calculations. *The Journal of Physical Chemistry C*. 2013;117(1): 22954-22966. DOI: 10.1021/jp407970a