Islamic Azad University

Journal of
Optoelectronical Nanostructures

Winter 2022 / Vol. 7, No. 1

Research Paper

Carbon Monoxide Gas Sensor Based on $ZrSe_2$ Monolayer Nanosheet

Soroush Karimi Khorrami[1], Masoud Berahman*[,2], Mojtaba Sadeghi[1]

[1] Department of Electrical Engineering, Shiraz Branch, Islamic Azad University, Shiraz, Iran

[2] Department of electrical Eng., Graduate University of Advanced Technology, Kerman, Iran.

Received: 23 Dec. 2021
Revised: 14 Jan. 2022
Accepted: 20 Feb. 2022
Published: 5 Mar. 2022

Use your device to scan and read the article online

Keywords:
Transition Metal Dichalcogenides, $ZrSe_2$ Nanosheet, CO Gas Molecule,Density Functional Theory

Abstract: Recently, the semiconducting electronic properties of different compounds of two-dimensional (2D) materials have been explored. One of the most important members of this family (ZrSe2; Zirconium diselenide) is used to substitute the silicon in Nano electronics because of its considerable bandgap. Moreover, this material seems to have potential application in sensing some toxic gases. In this research, we have investigated the adsorption ability of ZrSe2 nanosheet structure when the CO and CO_2 gas molecules are applied to the nanosheet surface. The simulation results show appropriate and considerable sensing property of this structure in presence of CO gas molecule with stable configuration and prominent changes in amount of current after gas adsorption. The CO gas molecule shows a stable and considerable adsorption on the $ZrSe_2$ structure which indicates that the $ZrSe_2$ nanosheet structure is a proper case for gas sensing applications. I-V calculations illustrate a selective sensitivity to this especial gas molecule.

Citation: Soroush Karimi Khorrami, Masoud Berahman, Mojtaba Sadeghi. Carbon Monoxide Gas Sensor Based on ZrSe2 monolayer nanosheet. **Journal of Optoelectronical Nanostructures. 2022; 7 (1): 55- 66.**
DOI: 10.30495/JOPN.2022.29652.1250

***Corresponding author:** M.Berahman. **Address:** Department of Electrical Eng, Graduate University of Advanced Technology, Kerman, Iran.
Tell: 00983433776611 **Email:** m.berahman@kgut.ac.ir

1. INTRODUCTION

Carbon monoxide is a colorless, odorless gas with CO formula. The exposure limit for 8 hours to this gas is as low as 35 ppm and the immediate reaction is 70 ppm which exposing to it shows headache and fatigue symptoms in human. The 150 ppm or above concentration of carbon monoxide is lethal for human [1]. In addition, the estimate rate for CO poisoning in Iran is about 38 for 10000 [2], which indicate the importance of monitoring this gas molecule in technology and indoors with low power and high sensitivity. There are various techniques that can be used to achieve such goal; including chemi-resistance, gas chromatography and spectroscopic methods [3]. Among them, chemi-resistance has introduced itself as a promising one. However, using new materials such as two-dimensional materials may even improve these sensors to detect molecular concentration of carbon monoxide.

Two-dimensional transition-metal dichalcogenides (TMDs) of IVB-VIA group are introduced itself as promising family of 2D materials due to its unique electrical and optical properties. They has been used in various potential applications such as photodetectors [4], photo electrochemical devices [5], the p–n junctions [6], logic transistors [7] and field-effect transistors (FETs) [8] and, sensors [9]. There are numerous reports that used TMDs for detecting molecular concentration of gas in an environment [10].

ZrX_2 (X=S and Se) are the members of two-dimensional transition-metal dichalcogenides which has considerable covalent inter layer interactions with weak van der Waals interactions between layers. The previous studies show that all ZrX_2 structures are semiconductors and also their band gaps vary between visible-infrared ranges; as a result, they can be suitable candidates for different electronic applications such as photovoltaic applications [11].

According to previous studies, Zhao et al. [12] have studied the electronic properties of $ZrSe_2$ monolayer structure and doped $ZrSe_2$ monolayer structures

with different materials such as N, P and Mn. Their findings shows the nonmagnetic metallic behaviors of N-doped, P-doped, and (N, P)-codoped (doped with N and P atoms) systems and magnetic semiconducting behavior of Mn-doped $ZrSe_2$ structure. Moreover, both (Mn, N) and (Mn, P)-codoped structures illustrate the metallic behavior [12].

In another research, the electronic properties of sandwiched transition-metal dichalcogenides such as ZrS_2, $ZrSe_2$, HfS_2, and $HfSe_2$ have been investigated. The density of states calculations show that the transition metal atoms affect the conduction band and on the other hand, the chalcogenide atoms change the valence band significantly [13].

To the best of our knowledge, there has been no published research in the field of sensing properties of $ZrSe_2$ structure. Also, The Zirconium diselenide is an applicable material to substitute the silicon in nanoelectronics because of its suitable gap. The main purpose of our article is to evaluate the effect of CO and CO_2 gas molecules on electronic properties of $ZrSe_2$ nanosheet.

The rest of paper is outlined as: in the section 2, we present the method and math details. Then, in the part 3, we gather and explain the main results, and in the part 4, the main conclusion is discussed.

2. MATH

The origin calculations and methods are exerted under the frame of density functional theory (DFT) [14, 15] in the SIESTA package [16]. For all the calculations, the Perdew, Burke, and Ernzerhof (PBE) exchange correlation of the generalized gradient approximation (GGA) is used [17-22]. Double zetta polarized basis set is adopted for all the atoms. The relaxation threshold of energy is considered as 0.0001 eV and the Hellmann–Feynman force between relevant atoms is adjusted to be less than $0.01 eVA^{-1}$. The 1×11×11 k-sample based on gamma-centered method is used for sampling the Brillouin zones with 300 Ry amount of mesh cut-off energy. The green function tuned with DFT is

used to calculate the transport properties as implemented in TranSIESTA package [16]. The 1×2×130 k-point sample is used to simulate the transport properties of relevant structures.

3. RESULTS AND DISCUSSIONS

The atomic structure of $ZrSe_2$ nanosheet should be fully relaxed to find the most stable relevant structure. Then, the mentioned gas molecules are located at different sites above $ZrSe_2$ nanosheet structure. The simulations result in the values of Fermi energy, the band gap energy, the adsorption energy and the interaction distance (the distance of the closest atoms between $ZrSe_2$ structure and gas molecules). The adsorption energy formulation is as follows:

$$\mathrm{Eads} = \mathrm{E}(\mathrm{ZrSe_2} + gasmolecule) - E(ZrSe_2) - E(gasmolecule) \quad (1)$$

Where $\mathrm{E}(\mathrm{ZrSe_2} + gasmolecule)$, $\mathrm{E}(\mathrm{ZrSe_2})$ and $\mathrm{E}(gasmolecule)$ are the total energies of $ZrSe_2$ with adsorbed gas molecule systems, individual $ZrSe_2$ systems and gas molecule, respectively.

1) $ZrSe_2$ nanosheet structure with CO gas molecule

In order to investigate the CO gas molecule adsorption on $ZrSe_2$ nanosheet structure, first, a gas molecule is located at different positions like above zirconium or selenium atoms, above the center of a honey comb structure and above the center of Zr-Zr/ Se-Se/ Zr-Se bonds. Plus, for relevant gas molecule three major directions are considered such as parallel, perpendicular with C atom toward $ZrSe_2$ surface and perpendicular with O atom toward $ZrSe_2$ surface.

As illustrated in figures 1 and 2, the most stable configurations for $ZrSe_2$ structure with or without CO gas molecule are achieved (in the initial structure CO gas molecule is placed above a zirconium atom with C atom toward the $ZrSe_2$ surface). Moreover, the adsorbed C-O axis aligned perpendicular with C atom head to structure with respect to $ZrSe_2$ surface. In other words, the CO gas

molecule bonds with $ZrSe_2$ surface significantly. The results show that the distance between the Zr atom of $ZrSe_2$ and the C atom of gas molecule is equal to 2.33A°. The Fermi, bandgap and adsorption energies of $ZrSe_2$ structure with CO gas molecule ($ZrSe_2$ structure) obtained as -4.693 eV (-4.466 eV), 0.62 eV (0.59 eV) and -0.84 eV, respectively. The negative low adsorption energy and small distance show a strong interaction between the $ZrSe_2$ structure and CO gas molecule.

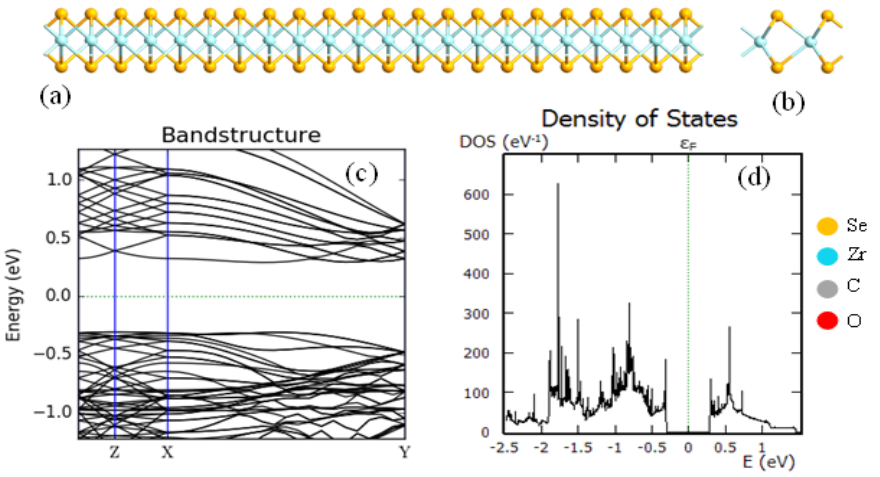

Fig. 1. The optimized structure and electronic properties of $ZrSe_2$ nanosheet, a) front view, b) side view, c) band structure, d) density of states (DOS) of the $ZrSe_2$ nanosheet structure.

In order to evaluate the adsorption effects of CO gas molecule on $ZrSe_2$ structure, the total density of states (DOS) and the band structures of relevant structures are calculated and illustrated in figures 1 and 2. In both cases, the band structure and DOS are in good agreement with the semiconducting behavior of both structures.

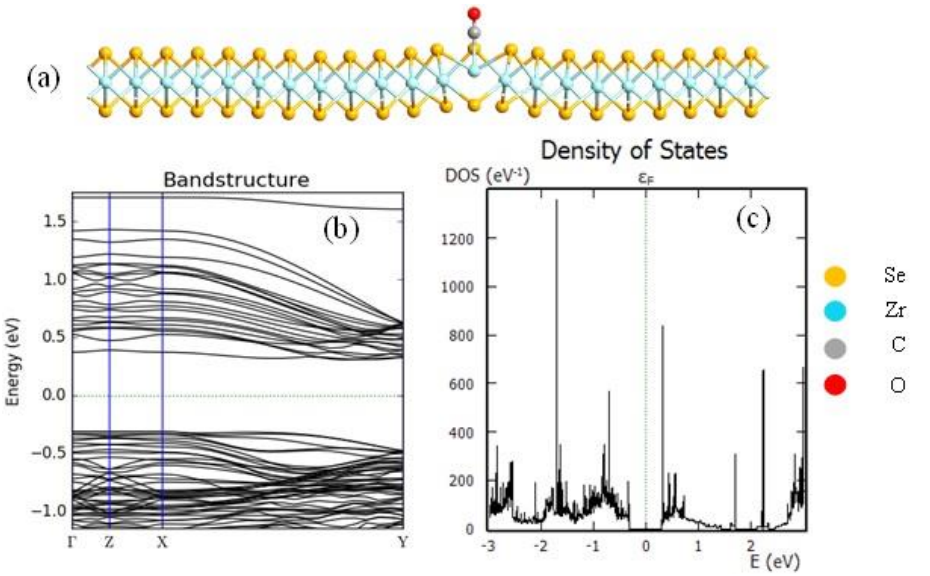

Fig. 2. The relaxed final structure of $ZrSe_2$ nanosheet with CO gas molecule, b) the band structure diagram, c) the DOS analysis of the $ZrSe_2$ nanosheet structure with CO gas molecule.

2) $ZrSe_2$ nanosheet structure with CO_2 gas molecule

In this step, the adsorption of CO_2 gas molecule on the $ZrSe_2$ nanosheet structure is investigated in detail. For this goal, CO_2 gas molecule is first located at different positions like above a zirconium/selenium atom, at the center of a honey comb structure and above the center of Zr-Zr/ Se-Se/ Zr-Se bonds.

The most stable configuration of $ZrSe_2$ structure with CO_2 gas molecule is illustrated in figure 3 (in the initial structure CO_2 gas molecule is placed above a selenium atom with O atom toward the $ZrSe_2$ surface). Plus, the adsorbed O-C-O axis aligned with the approximate angle of 29.06 degree with respect to the $ZrSe_2$ surface. In fact, the CO_2 gas molecule doesn't bond with $ZrSe_2$ surface and locates about 3.34 A° far from the underneath surface. The Fermi, bandgap and adsorption energies of $ZrSe_2$ structure with CO_2 gas molecule are as -4.70 eV, 0.60eV and -0.232 eV, respectively. The negative low adsorption energy and

large distance illustrate a relative weak interaction between the $ZrSe_2$ structure and CO_2 gas molecule compared with CO gas molecule.

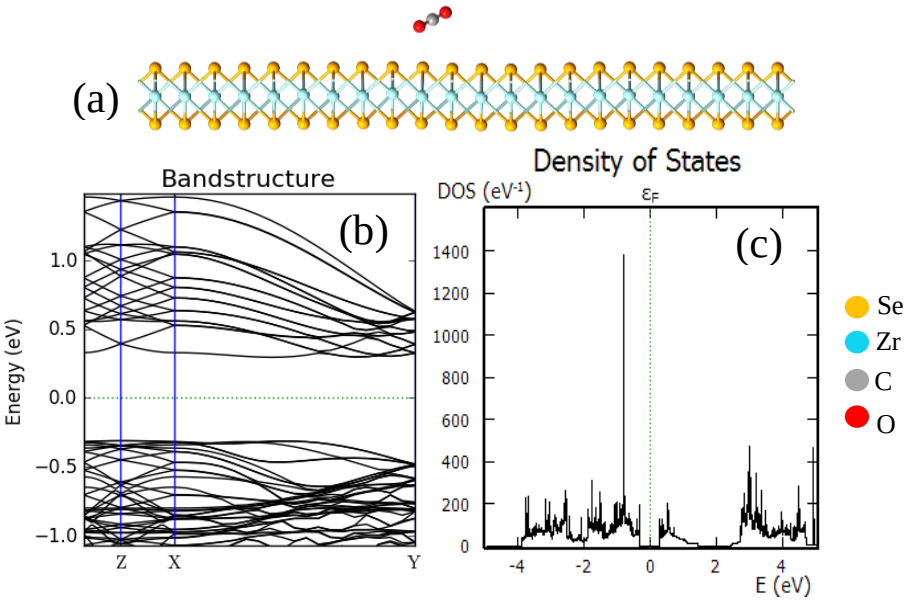

Fig. 3. a) The optimized structure of $ZrSe_2$ nanosheet in presence of CO_2 gas molecule, b) the band structure analysis, c) the DOS analysis of the $ZrSe_2$ nanosheet structure with CO_2 gas molecule.

To evaluate the effects of CO_2 gas adsorption onto the $ZrSe_2$ structure, the electronic properties such as the total electronic density of states (DOS) and the band diagram are calculated and shown in figure 3. The band structure and DOS are in good agreement with the semiconducting behavior of relevant structure.

3) The I-V characteristics and sensitivity of $ZrSe_2$ nanosheet structure with CO and CO_2 gas molecules

The interaction between CO gas molecules and $ZrSe_2$ nanosheet structure is highly likely able to alter the electrical properties of this structure, which can be the influence of gas molecule on electronic configuration of the device. Obviously, strong interactions cause considerable evolutions in electrical

conductivity, which is applicable and useful for sensing applications. On the other hand, the approximate weak interaction between CO_2 gas molecule and $ZrSe_2$ structure might not be significant enough to make any sense.

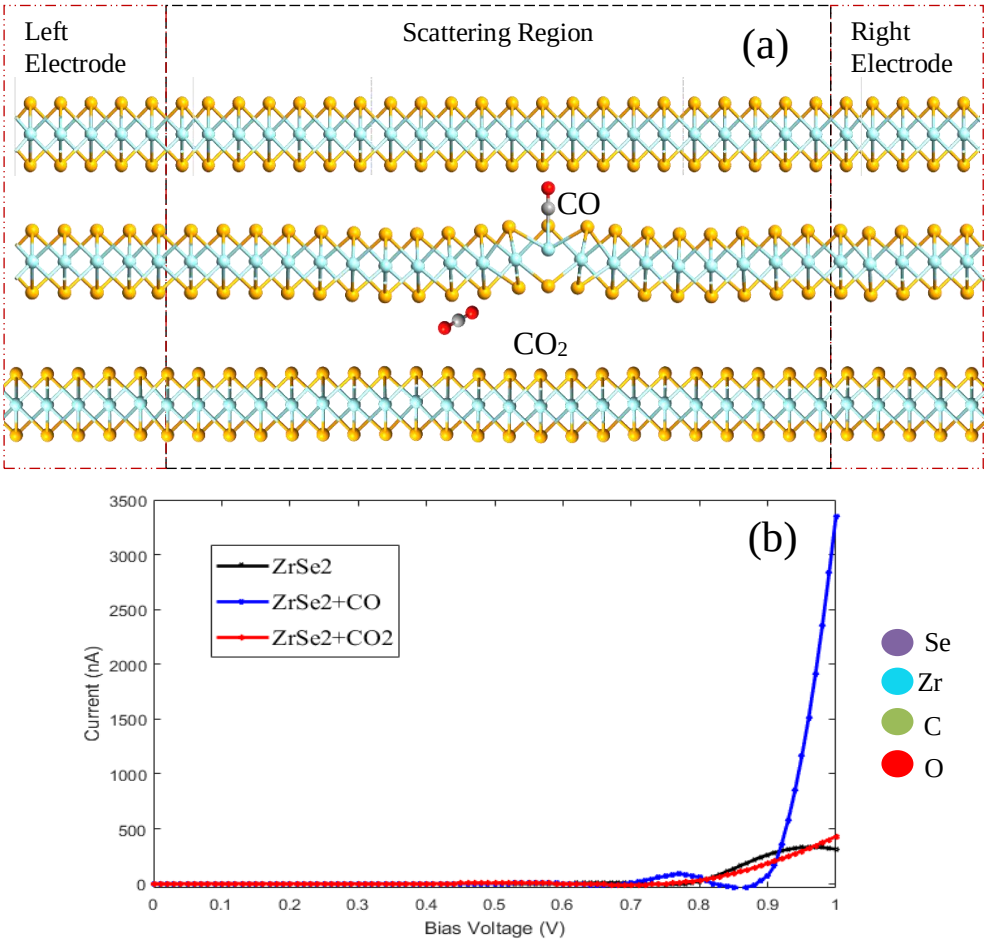

Fig. 4. a) The device of $ZrSe_2$ nanosheet with and without CO and CO_2 gas molecules, b) the comparison between I-V characteristics of $ZrSe_2$ nanosheet and $ZrSe_2$ nanosheet with CO and CO_2 gas molecules.

The I-V characteristics results show that after adsorbing CO and CO2 gas molecules onto ZrSe2 nanosheet structure, the current of all structures is zero until the bias voltage increases to 0.7- 0.8 V. Afterwards, under 0.9- 1.0 V, the

current of ZrSe2 nanosheet structure in presence of CO gas molecule rises drastically. So, this raised value becomes the largest value under 1.0 V and the difference between current of structures is very significant as shown in figure 4. It is deduced that the amount of sensitivity of ZrSe2 nanosheet structure toward CO gas molecule occurs between 0.9- 1.0 V. Moreover, ZrSe2 nanosheet structure can be a proper and selective gas sensor for CO gas molecule.

4. CONCLUSION

To conclude, the adsorption of CO and CO_2 gas molecule on the $ZrSe_2$ nanosheet structure has been investigated in detail. The CO gas molecule illustrates a stable and considerable adsorption on the $ZrSe_2$ structure because of negative large adsorption energy and small interaction distance, which shows that the $ZrSe_2$ nanosheet is a proper semiconductor for gas sensing applications. On the plus side, the I-V calculations show a selective sensitivity to this especial gas (CO gas molecule) at a specific applied voltage (0.9-1 V). In other words, this research introduces the $ZrSe_2$ nanosheet structure as a useful sensitive gas sensor.

REFERENCES

[1] https://www.cdc.gov/niosh/npg/npgd0105.html.

[2] https://pubmed.ncbi.nlm.nih.gov/29220732.

[3] https://www.ncbi.nlm.nih.gov/books/NBK153686.

[4] O. Lopez-Sanchez, D. Lembke, M. Kayci, A. Radenovic, and A. Kis, *Ultrasensitive photodetectors based on monolayer* MoS_2, Nature Nanotechnol. 8 (2013, Jul.), 497, doi: 10.1038/nnano.2013.100. Epub 2013 Jun 9.

[5] R. Tenne and A. Wold, *Passivation of recombination centers in n-WSe2 yields high efficiency (>14%) photoelectrochemical cell*, Appl. Phys. Lett. 47 (1985, Jul.), 707, https://doi.org/10.1063/1.96066.

[6] B. W. Baugher, H. O. Churchill, Y. Yang, and P. Jarillo- Herrero, *Optoelectronic devices based on electrically tunable p–n diodes in a monolayer dichalcogenide*, Nature Nanotechnol. 9 (2014, Mar.), 262-267, https://doi.org/10.1038/nnano.2014.25.

[7] R. Chau, S. Datta, M. Doczy, B. Doyle, B. Jin, J. Kavalieros, A. Majumdar, M. Metz, and M. Radosavljevic, *Benchmarking nanotechnology for high-performance and low-power logic transistor applications*, IEEE Trans. Nanotechnol. 4 (2005, Mar.), 153-158, DOI: 10.1109/TNANO.2004.842073.

[8] S. Z. Butler, S. M. Hollen, L. Cao, Y. Cui, J. A. Gupta, H. R. Gutierrez, T. F. Heinz, S. S. Hong, J. Huang and A. F. Ismach, Progress, *Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene*, ACS Nano 7 (2013, Mar.), 2898-2926, https://doi.org/10.1021/nn400280c.

[9] S. Kumar, V. Pavelyev, P. Mishra, N. Tripathi, P. Sharma, F. Calle, *A review on 2D transition metal di-chalcogenides and metal oxide nanostructures based NO2 gas sensors, Materials Science in Semiconductor Processing*, Volume 107 (2020, Mar.), 104865, ISSN 1369-8001, https://doi.org/10.1016/j.mssp.2019.104865.

[10] A. Shokri, N. Salaami, *Gas sensor based on MoS_2 monolayer*, Sensors and Actuators B: Chemical. 236 (2016, Jun.). Doi:10.1016/j.snb.2016.06.033.

[11] M. Moustafa, T. Zandt, C. Janowitz, and R. Manzke, *Growth and band gap determination of the $ZrSxSe_{2-x}$ single crystal series*, Phys. Rev. B 80 (2009, Jul.), 035206, doi: 10.1103/PhysRevB.80.035206.

[12] X. Zhao et al., *Modulating the electronic and magnetic properties of monolayer $ZrSe_2$ by doping*, Superlattices and Microstructures, 120 (2018, Jun.), 659-669, https://doi.org/10.1016/j.spmi.2018.06.038.

[13] Q. Zhao, Y. Guo, Keyu Si, Z. Ren, J. Bai, and X. Xu, *Elastic, electronic, and dielectric properties of bulk and monolayer ZrS_2, $ZrSe_2$, HfS_2, $HfSe_2$ from van der Waals density-functional theory*, Phys. Status Solidi B (2017, May), 1700033, doi: 10.1002/pssb.201700033.

[14] P. Hohenberg and W. Kohn, *Inhomogeneous Electron Gas*, Phys. Rev. 136 (1964, Nov.), B864, https://doi.org/10.1103/PhysRev.136.B864.

[15] W. Kohn and L. J. Sham, *Self-Consistent Equations Including Exchange and Correlation Effects*, Phys. Rev. 140 (1965, Nov.), A1133, https://doi.org/10.1103/PhysRev.140.A1133.

[16] V. McCann, V. I. Fal'ko, *Landau-Level degeneracy and quantum Hall effect in a graphite bilayer*, Phys. Rev. Lett. 96 (2006, Mar.), 086805, https://doi.org/10.1103/PhysRevLett.96.086805.

[17] J. P. Perdew, K. Burke, and M. Ernzerhof, *Generalized Gradient Approximation Made Simple*, Phys. Rev. Lett. 77 (1996, Oct.), 3865-3868, doi: 10.1103/PhysRevLett.77.3865.

[18] T. Niazkar, G. Shams, Z. soltani, *Electronic, Optical, and Thermoelectric Properties of BaFe2-xZnxAs2(x=0,1,2) orthorhombic Polymorphs: DFT Study*, Journal of Optoelectronical Nanostructures, 6(3) ((2021, Summer), 93-116. doi: 10.30495/jopn.2021.28945.1237.

[19] M. Dehghan, S. Ahmadi, *Adsorption Behaviour of CO Molecule on Mg16M—O2 Nanostructures (M=Be, Mg, and Ca): A DFT Study*, Journal of Optoelectronical Nanostructures, 6(1) (2021, Winter), 1-20, doi: 10.30495/jopn.2021.4538.

[20] S. Fotoohi, S. Haji Nasiri, *Vacancy Defects Induced Magnetism in Armchair Graphdiyne Nanoribbon*, Journal of Optoelectronical Nanostructures (2019, Autumn) 4(4), 15-38, https://dorl.net/dor/20.1001.1.24237361.2019.4.4.2.6.

[21] S. Mousavi, *First–Principle Calculation of the Electronic and Optical Properties of Nanolayered ZnO Polymorphs by PBE and mBJ Density*

Functionals, Journal of Optoelectronical Nanostructures (2017, Autumn) 2(4), 1-18, https://dorl.net/dor/20.1001.1.24237361.2017.2.4.1.1.

[22] H. Salehi, P. Amiri, R. zare Hasanabad, *Ab-initio study of Electronic, Optical, Dynamic and Thermoelectric properties of CuSbX2 (X=S,Se) compounds*, Journal of Optoelectronical Nanostructures (2018, Spring) 3(2), 53-64, https://dorl.net/dor/20.1001.1.24237361.2018.3.2.5.8.