Simulation of NO_2 work function-based sensor signal on ZnO

Simulation of NO_2 work function-based sensor signal on ZnO

R. Marjunus[1,*], D. C. Kekalenteu[1], A. Riyanto[1], W. Widanarto[2]

[1]University of Lampung, Jl. Prof. Dr. Soemantri Brodjonegoro No.1, Bandar Lampung 35145, Indonesia
[2]University of Jenderal Soedirman, Jl. Profesor DR. HR Boenyamin No.708, Dukuhbandong, Grendeng, Kec. Purwokerto Utara, Kabupaten Banyumas, Jawa Tengah 53122

email:roniyus.1977@fmipa.unila.ac.id[1,*]

Abstract. Simulation of sensor signal based on the ZnO work function for NO_2 gas has been conducted. This research is aimed at approaching the experiment results of nitrogen dioxide (NO_2) gas detection using the ZnO sensor. This study uses three reactions i.e., adsorption-desorption of O_2 (oxygen), adsorption-desorption of NO_2, and the reaction of O_2 and NO_2 on ZnO. This simulation has optimized 12 parameter values that are responsible for those reactions. After the optimized values were obtained, the final simulation was reached. The final simulation still cannot perfectly fit the experiment results because of the number of reactions which are used still three reactions. It is predicted, if it is used much more reactions, the simulation could be the same as the experiment results. Although this simulation is still not same as the experiment result, it has a trend as the experiment result. The last result of this model i.e. it can predict the coverage of O atom, O_2 molecule, and NO_2 molecule.

1. Introduction

The earth's surface is covered by the atmosphere, a layer of gas that covers each planet that's dominated by nitrogen and oxygen. These elements can react to each other to produce nitrogen dioxide (NO_2) gas. It can also be triggered by fossil fuel combustion [1]. NO_2 is a reddish-brown gas and has a pungent odor [2]. This gas can be toxic for humans, especially to the lungs, because it can harm the respiratory system [3]. Moreover, the gas also can cause the photosynthesis ability of plants to decrease and acid rain for the environment [4].

A lot of researches regarding detection of NO_2 gas have been done; one of them is using a zinc oxide (ZnO) sensor. In 2010, Spencer revealed that N and O are chemically absorbed and stable on the surface up to 700 K. Furthermore, NO_2 stability on the surface can be increased by the presence of oxygen [5]. Then, in 2011 Widanarto succeeded producing a NO_2 gas sensor using the Floating Gate Field Effect Transistor (FG-FET) system with ZnO as the sensitive layer [6]. This sensor shows work function change ($\Delta\phi$) when the sensitive layer is exposed to the NO_2. Work function is the minimum energy to release the electrons from its Fermi level energy [7].

In the process of NO_2 detection, there are several chemical reactions occurring, started from adsorption, dissociation, and desorption [8]. The first adsorption process is the adsorption of oxygen molecules onto

the material surface and then forms oxygen anions ($2O^-_{(s)}$). This adsorption process is shown in Equation (1),

$$O_{2(g)} + S \rightleftharpoons O_{2(s)}. \quad (1)$$

Furthermore, when NO_2 gas is exposed to ZnO sensor material surface, the gas will be adsorbed as presented in Equation (2),

$$NO_{2(g)} + S \rightleftharpoons NO_{2(s)}. \quad (2)$$

After that, there will be an interaction between O and NO_2 which are on the sensitive layer surface as is given by the Equation (3),

$$O_{(s)} + NO_{2(s)} \rightleftharpoons O_{2(s)} + NO_{(s)}. \quad (3)$$

In the chemical reaction, there are known various parameters, such as activation energy, sticking coefficient, and Arrhenius coefficient. The activation energy (E) is the minimum energy which is needed to carry out a reaction, sticking coefficient (S) is the ratio between particles that are bound on the surface and the particles come to it, and the Arrhenius coefficient (υ) shows the effect of temperature changes which indicates the rate of reaction [9]. Since the parameter values of Equation (1) – (3) on ZnO are poor, some values are taken from the same reactions but different sensitive layer [10, 11]. So, the values are as shown in Table 1.

Table 1. The initial value of reaction parameters for NO_2 gas detection

Equation Number of Reaction	Forward Reaction		Reverse Reaction	
	S_0 & υ (s^{-1})	E_f (eV)	S_0 & υ (s^{-1})	E_r (eV)
1	$S_0 = 10^{-6}$	0,53	$\upsilon = 8{,}0515 \times 10^{12}$	$2{,}20966 - 0{,}622\ \Theta_o$
2	$S_0 = 0{,}3$	0,47	$\upsilon = 0{,}3$	0,47
3	$\upsilon = 8{,}0515 \times 10^{12}$	-	$\upsilon = 8{,}0515 \times 10^{12}$	-

Θ_o is the coverages of O atom on the catalyst surface [12].

2. Simulation Method

This simulation begins with the formation of differential equations from Equation (1) – (3). Then, the step is continued by fitting the experimental data, which was obtained by Widanarto et al. as the reference data [7]. Fitting is necessary in order to find the mean error of $\Delta\phi$ between Widanarto's experiment and the simulation. The simulation starts with completing the data in Table 1 by finding the activation energy for the interaction between NO_2 and O (E_{f3} dan E_{r3}). After obtaining E_{f3} and E_{r3}, the simulation is continued by optimizing the parameter values which have been obtained before. This step is done in order to find the best value of each parameter because these values are not originally for ZnO. Optimization is done sequentially, starting from the adsorption energy of O_2 and NO_2 (E_{f1} and E_{f2}), then the desorption energy of O and NO_2 (E_{r1} and E_{r2}), followed by the sticking coefficient for O_2 (S_1) and NO_2 (S_2). Then, the optimization is continued by the Arrhenius coefficient of the interaction between O and NO_2 (υ_{f3}), the reverse reaction of their interaction (υ_{r3}), O_2 desorption (υ_{r1}), and NO_2 desorption (υ_{r2}). After all of the parameters are optimized and obtained the best values of them, it is needed to re-optimize the data from the beginning in order to find out whether the parameter values are independent or not.

3. Results and Discussion

3.1 Differential Equation

Based on Equation (1) – (3), it can be arranged the differential equation which is needed in this simulation as shown in Equation (4) – (7),

$$\frac{d\theta_{NO_2}}{dt} = r_{f2}F_{NO_2} - r_{f3}\theta_O\theta_{NO_2} + r_{r3}\theta_{O2}\theta_{NO} - r_{r2}\theta_{NO_2} \quad (4)$$

$$\frac{d\theta_O}{dt} = 2r_{f1}F_{O_2} - r_{f3}\theta_O\theta_{NO_2} + r_{r3}\theta_{O2}\theta_{NO} - 2r_{r2}\theta_{NO_2} \quad (5)$$

$$\frac{d\theta_{NO}}{dt} = r_{f3}\theta_O\theta_{NO_2} - r_{r3}\theta_{O2}\theta_{NO} \quad (6)$$

$$\frac{d\theta_{O2}}{dt} = r_{f3}\theta_O\theta_{NO_2} - r_{r3}\theta_{O2}\theta_{NO} \quad (7)$$

3.2. Experiment Data's Fitting

Experiment data fitting was carried out using polynomial, which showed the best fitting at order six and gave the result in Figure 1.

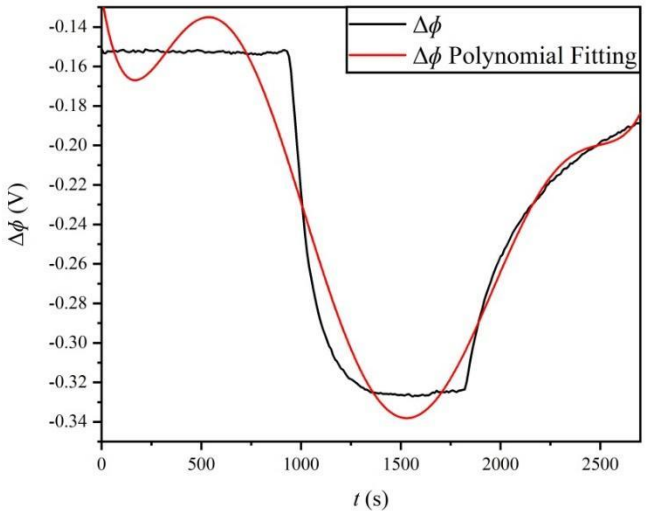


Figure 1. The polynomial fitting curve for experiment data.

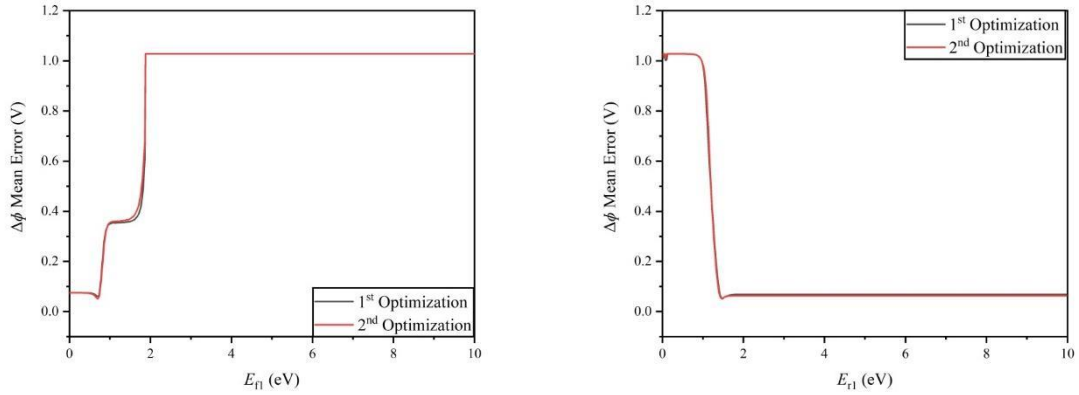
Fitting equation of Figure 1 is as given in Equation (8),

$$\Delta\phi = a_1t + a_2t^2 + a_3t^3 + a_4t^4 + a_5t^5 + a_6t^6 + a_7 \quad (8)$$

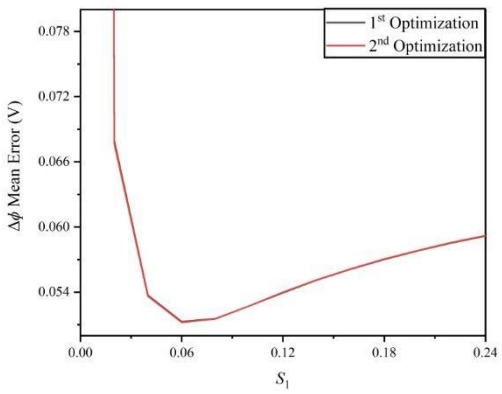
where a_1 = -6,09455 x 10^{-4} V, a_2 = 2,8141 x 10^{-6} V, a_3 = -4,67347 x 10^{-9} V, a_4 = 3,26098 x 10^{-12} V, a_5 = -1,01316 x 10^{-15} V, a_6 = 1,16501 x 10^{-19} V and a_7 = 0,1243 V.

3.3. Parameter Value Finding, First and Second Optimization

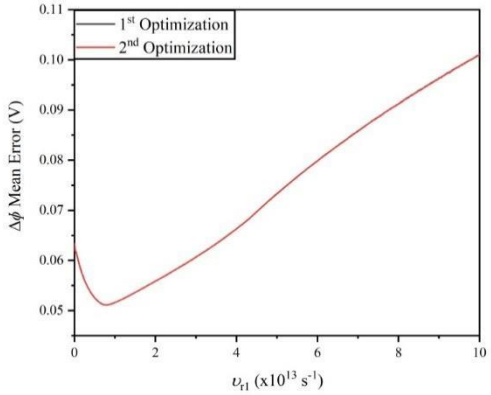
The results of parameter value finding, first and second optimization are as presented in Figure 2.



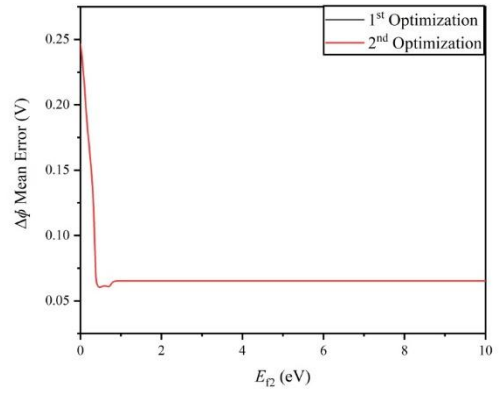
(a) (b)


1st Optimization
2nd Optimization
Δϕ Mean Error (V)
0.078
0.072
0.066
0.060
0.054
0.00
0.06
0.12
0.18
0.24
S_1

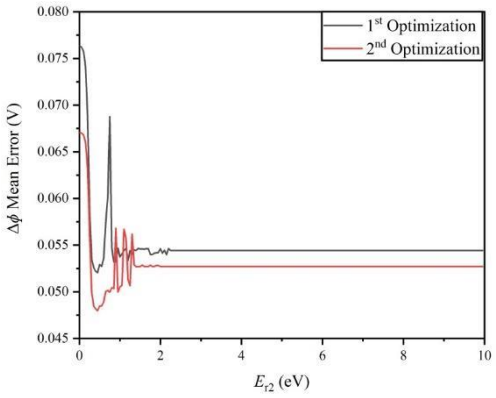
(c)


1st Optimization
2nd Optimization
Δϕ Mean Error (V)
0.11
0.10
0.09
0.08
0.07
0.06
0.05
0
2
4
6
8
10
υ_{r1} (x10^{13} s^{-1})

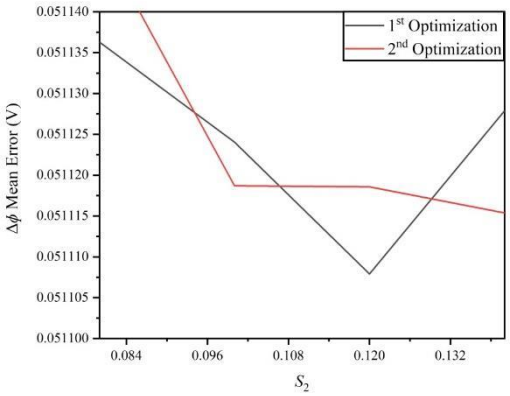
(d)


1st Optimization
2nd Optimization
Δϕ Mean Error (V)
0.25
0.20
0.15
0.10
0.05
0
2
4
6
8
10
E_{f2} (eV)

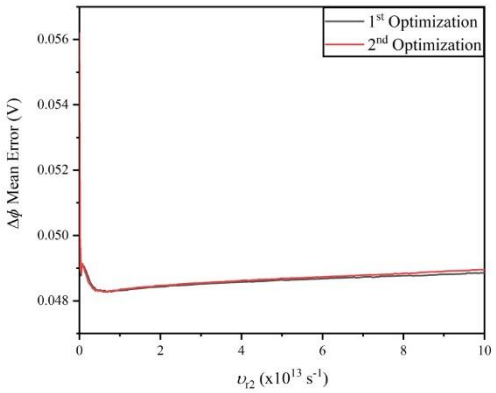
(e)


1st Optimization
2nd Optimization
Δϕ Mean Error (V)
0.080
0.075
0.070
0.065
0.060
0.055
0.050
0.045
0
2
4
6
8
10
E_{f2} (eV)

(f)


1st Optimization
2nd Optimization
Δϕ Mean Error (V)
0.051140
0.051135
0.051130
0.051125
0.051120
0.051115
0.051110
0.051105
0.051100
0.084
0.096
0.108
0.120
0.132
S_2

(g)


1st Optimization
2nd Optimization
Δϕ Mean Error (V)
0.056
0.054
0.052
0.050
0.048
0
2
4
6
8
10
υ_{f2} (x10^{13} s^{-1})

(h)

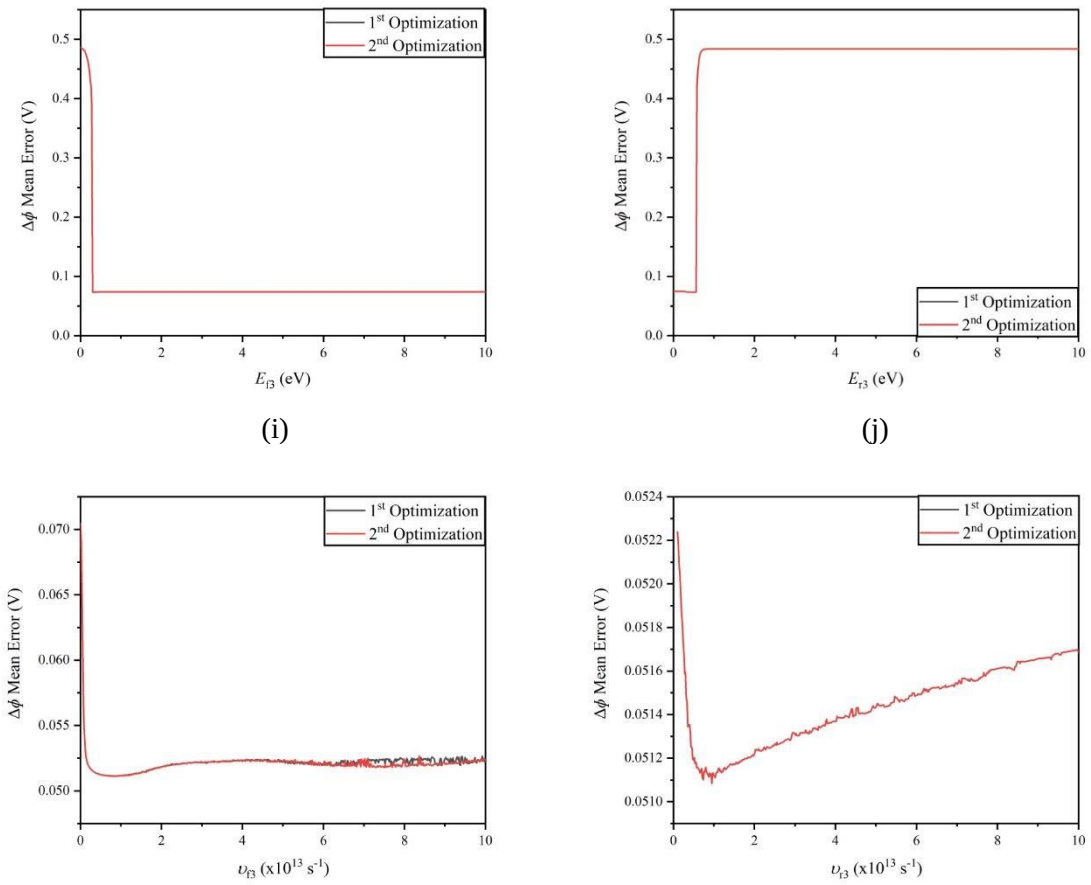


Figure 2. Comparison of First and Second Optimization

After the parameter value finding, first and second optimizations (Figure 3) were done, it results in the new parameter values given in Table 2.

Table 2. Optimized values of NO_2 detection reaction parameters

Reaction	Forward Reaction		Reverse Reaction	
	S_0 & υ (s^{-1})	E_f (eV)	S_0 & υ (s^{-1})	E_r (eV)
1	S_0 = 0,068	0,70	υ = 8 x 10^{12}	1,47
2	S_0 = 0,12	0,48	υ = 6,8 x 10^{12}	0,46
3	υ = 8,3 x 10^{12}	0,34	υ = 9,5 x 10^{12}	0,50

These optimized values in Table 2 are the best values that were obtained based on the smallest mean error of $\Delta\phi$. According to the second optimization also shows that after the re-optimization, there are no many differences between the first and second optimization, as shown in Figure 3. It proves the hypothesis that parameter values should be independent of each other. The parameter values depend only on the sensor material characteristic (ZnO, in this case) and the gas which interacts with the material (NO_2, in this case).

After the best values of the parameters were obtained, the simulation was done again in order to find the final result of the simulation, then compare it with the experiment result, as revealed in Figure 3.

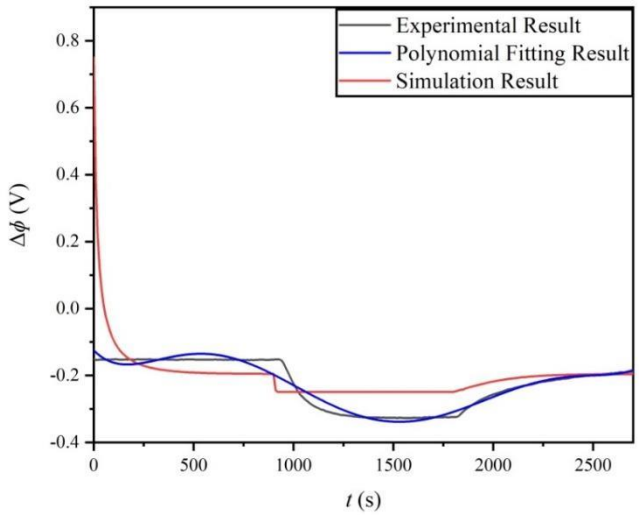
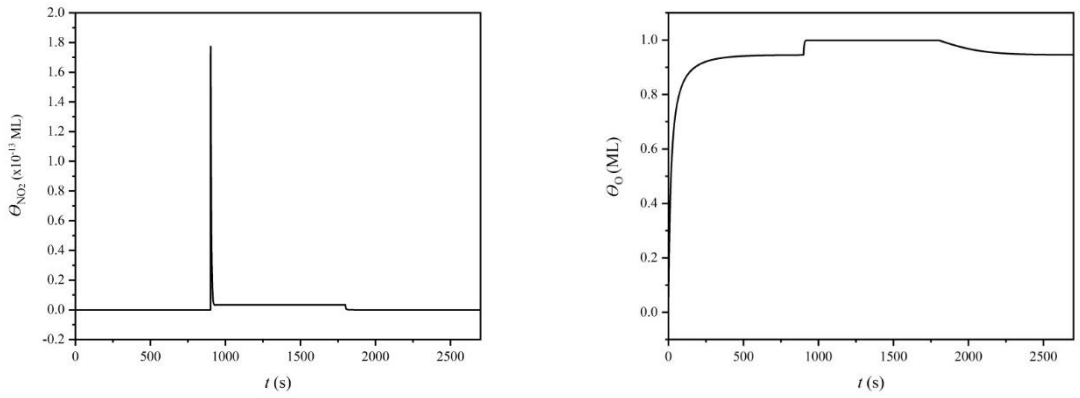


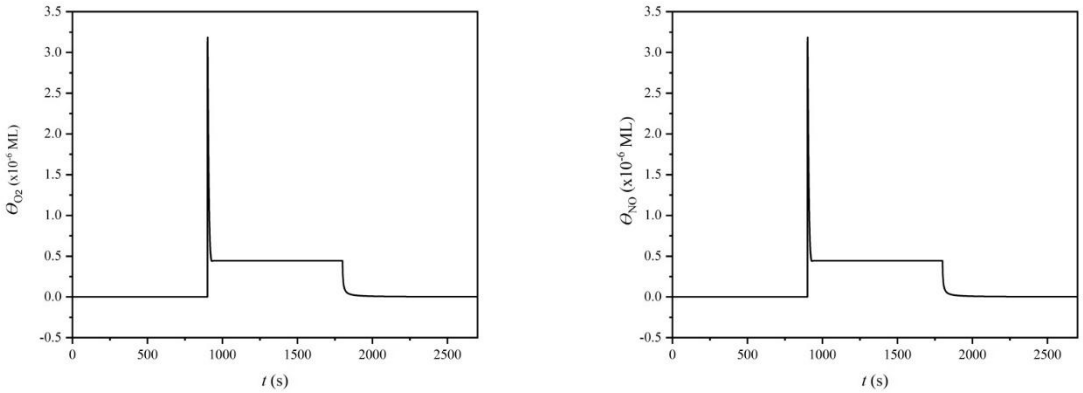
Figure 3. Comparison between experiment, fitting, and simulation.

Figure 3 shows the comparison result between the experiment with the fitting on it and the result from this simulation. Based on Figure 3, it can be seen; this simulation already has the same trend as the experiment result. The average error of work function change between simulation and experiment results is 0.447035 V. It also shows a significant difference between simulation and experiment results in the first 2 minutes. It occurs because the initial state of ZnO was without O exposure in the simulation, then exposed by O, it causes the work function of ZnO to decrease drastically. It does not occur in the experiment by Widanarto et al. (2011) [6]. In the experiment, ZnO has been exposed by O for a long time before, then in the moment of work function measurement is done during 15 minutes before NO_2 gas exposing, the work function of ZnO is already stable.

The imperfection of this simulation result also can be caused by the number of reference reactions. In this simulation, the reaction which is considered to be involved in NO_2 gas detection is three reactions. If many more reactions are involved, it could close the experiment result.



(a) (b)



(c) (d)

Figure 4. Simulated coverage of NO_2, O, O_2 and NO

According to Figure 4, it shows that NO_2 coverage (3×10^{-15}ML) is very low than O_2 (4×10^{-7}ML), NO (4×10^{-7}ML), and O (0,995 ML). These calculations indicate that the coverage of O plays the role of the work function change of ZnO. Although the coverage of the NO_2 is not much as O, the existence of NO_2 on the surface influences the coverage of O.

4. Conclusion

Based on the discussion of results, it can be concluded this simulation can be used to find the parameter values which are responsible at the NO_2 detection on ZnO, proves that parameter values are only influenced by the gas and the sensitive layer's characteristic, has already the same trend as the experiment result, shows the domination of O coverages, and the average error of work function change between simulation and experiment result is 0.447035 V.

5. References

[1] Beirle S, Platt U, Wenig M and Wagner, T Weekly cycle of NO_2 by GOME measurements: a signature of anthropogenic sources *Atmos. Chem. Phys.* **3** 2225 – 32

[2] Voiculescu M, Constantin D E, Condurache-Bota S, Călmuc V, Roșu A, Bălănică, C M D 2020 Role of meteorological parameters in the diurnal and seasonal variation of NO_2 in a romanian urban environment *Int. J. Environ. Res. Public Health* **17** 6228.

[3] Olivieri D and Scoditti E 2005 Impact of environmental factors on lung defences *Eur. Respir. Rev.* **14** 51- 6

[4] Qianqian S and Zhu Z 2018 Photosynthetic capacity, stomatal behavior and chloroplast ultrastructure in leaves of the Endangered Plant *Carpinus putoensis* W.C.Cheng during gaseous NO_2 exposure and after recovery *Forests* **9** 561 – 76.

[5] Spencer M J S and Yarovsky I 2010 ZnO Nanostructure for gas sensing : Interaction of NO_2, NO, O, and N with the ZnO. *J. Phys. Chem. C.* **114** 10881 – 10893.

[6] Widanarto W, Senft C, Senftleben O, Hansch W and Eisele I 2011 Characterization and sensing properties of ZnO film in FG-FET sensor system for NO_2 detection. *International Journal of Basic & Applied Sciences IJBAS-IJENS.* **11** 104 – 108.

[7] Senft C, Iskra P, Eisele I and Hansch W 2011 *Work Function – Based Sensor : Schottky and FET – Based Devices* (in Chemical Sensors: Comprehensive Sensor Technologies, Editor : G. Korotchenkov). Vol. 4. Momentum Press. New York.

[8] Somorjai G A and Li Y 2010 *Introduction to Surface Chemistry and Catalysis, Second ed.* John Wiley & Sons. New York.

[9] Nix R M 2014 *An Introduction to Surface Chemistry*. Queen Mary University of London. London.

[10] Qi P, Vermesh O, Grecu M, Javey A, Wang Q, Dai H, Peng S and Cho K J 2003 Toward large arrays of multiplex functionalized carbon nanotube sensors for highly sensitive and selective molecular detection *Nano Lett.* **03** 347 – 51.
[11] Nugraha, Saputro A G, Agusta M K, Yuliarto B, Dipojono H K and Maezono R 2016 Density functional study of adsorption of CO_2, NO_2 and SO_2 molecules on Zn(0002) surface *J. Phys: Conference Series* **739** 1 - 8.
[12] Marjunus R 2018 *Development of Pt-based Sensitive Layer for Carbon Monoxide Work Function Change Based Sensor in Air at Room Temperature* Dissertation Fakultät für Elektrotechnik und Informationstechnik, Universität der Bundeswehr München, Germany.