Journal of Engineering Science
Fascicle
Topic
Electronics and Computer Science
Computers and Information Technology
Vol. XXV (2) (2018), pp. 38-44
ISSN 2587-3474
eISSN 2587-3482

TEMPERATURE DEPENDENT GAS SENSING PROPERTIES OF TIN-DOPED ZINC OXIDE FILMS

Postica Vasile

Department of Microelectronics and Biomedical Engineering, Technical University of Moldova,
168 Stefan cel Mare Av., MD-2004 Chisinau, Republic of Moldova
Corresponding author: Postica Vasile, vasile.postica@mib.utm.md

Received: May, 10, 2018
Accepted: June, 30, 2018

Abstract. In this work, the temperature dependent gas sensing properties of tin-doped zinc oxide (ZnO:Sn) nanostructured films are investigated in detail. The two different contents of Sn in ZnO:Sn samples (0.1 and 0.4 at% Sn) and rapid thermal annealing (RTA) at 725 ºC were used, in order to find out the optimal conditions for the highest gas sensing properties, i.e. higher gas response, selectivity and lowest operating temperature. Generally, the Sn-doped ZnO nanostructured films showed high selectivity to volatile organic compounds (VOCs) vapors, such as ethanol, acetone, 2-propanol and *n*-butanol, compared to different reducing gases such as H_2, NH_3 and CH_4. The optimal operating temperature for all films is 250 – 300 ºC and the optimal content of Sn is 0.4 at%. The as-grown films showed higher gas response compared to RTA treated ones. The gas sensing mechanism was proposed and discussed in detail.

Keywords: *gas sensor, volatile organic compounds, zinc oxide, nanostructured films*

Introduction

VOCs are organic chemicals that have a high vapor pressure at room temperature. The detection of VOCs is one of the main tasks for indoor air quality control due to regulations in many countries of the world [1, 2]. Nowadays, many of people spend most of their day indoors. Therefore, the poor air quality is a serious risk which may cause short-term health problems. It has been demonstrated that the real-time monitoring with low-cost and robust sensors can be performed using micro- and nanostructured of metal oxides such as ZnO, SnO_2, etc. [3, 4]. These materials can efficiently detect a wide range of VOCs relevant to environmental monitoring such as ethanol, acetone, 2-propanol, methanol, *n*-butanol, hexane, benzene, xylene, etc. at relative low concentrations (ppb – sub-ppm level) [4 - 7]. Another important advantage of these oxide materials is the possibility to fabricate compact size and portable devices with low power consumption [7, 8].

Another application for VOCs sensors is the noninvasive breath analysis for diagnostic of metabolic diseases, which has attracted a considerable amount of scientific and clinical interest during the last decade due to rapid progress of nanotechnologies [9, 10]. Many studies demonstrated that different types of exhaled VOCs vapors have correlations with different diseases [11-13]. Recently, 17 diseases were diagnosed and classified from 1404 subjects via pattern analysis of exhaled molecules based on artificial intelligent nanoarray with an accuracy of 86% [11]. As an example, acetone in the human

breath is an important marker for noninvasive diagnosis of diabetes [12]. Therefore, the development of high performance portable VOCs sensors is very important for many fields. In this work, the VOCs sensing properties of Sn-doped ZnO nanostructured films is reported in detail, and demonstrated high sensitivity and selectivity to a series of low concentrations of VOCs vapors (ethanol, acetone, 2-propanol, *n*-butanol, methanol) at 250 – 300 ºC operating temperature.

Experimental part

The Sn-doped ZnO nanostructured films were growth on glass substrates via a SCS approach from aqueous baths. The experimental conditions for growth of ZnO:Sn samples is described in previous work [14]. To achieve the concentration of 0.1 and 0.4 at% Sn, 2.5 and 11.5 mM of tin(II) sulfate $[SnSO_4]$ was added in the complex solution [14]. The morphological, structural, chemical, electrical and UV sensing properties are reported in detail in our previous work [14]. In this work, only temperature dependent gas sensing properties of the ZnO:Sn nanosensor will be investigated. The thickness of films used in this study is 1.5 ± 0.15 μm. The as-grown films were exposed to rapid thermal annealing (RTA) treatment at 725 ºC for 60 s. The gas sensing investigations were performed as described previously [15 - 17].

Results and discussions

First of all, we will investigate the influence of Sn content on gas response of ZnO:Sn films. Figure 1a and 1b shows the gas response versus operating temperature for as-grown samples with 0.1 and 0.4 at% Sn, respectively. The gas response is calculated as the ratio of current under gas exposure (I_{gas}) and under exposure to ambient air (I_{air}). The concentration

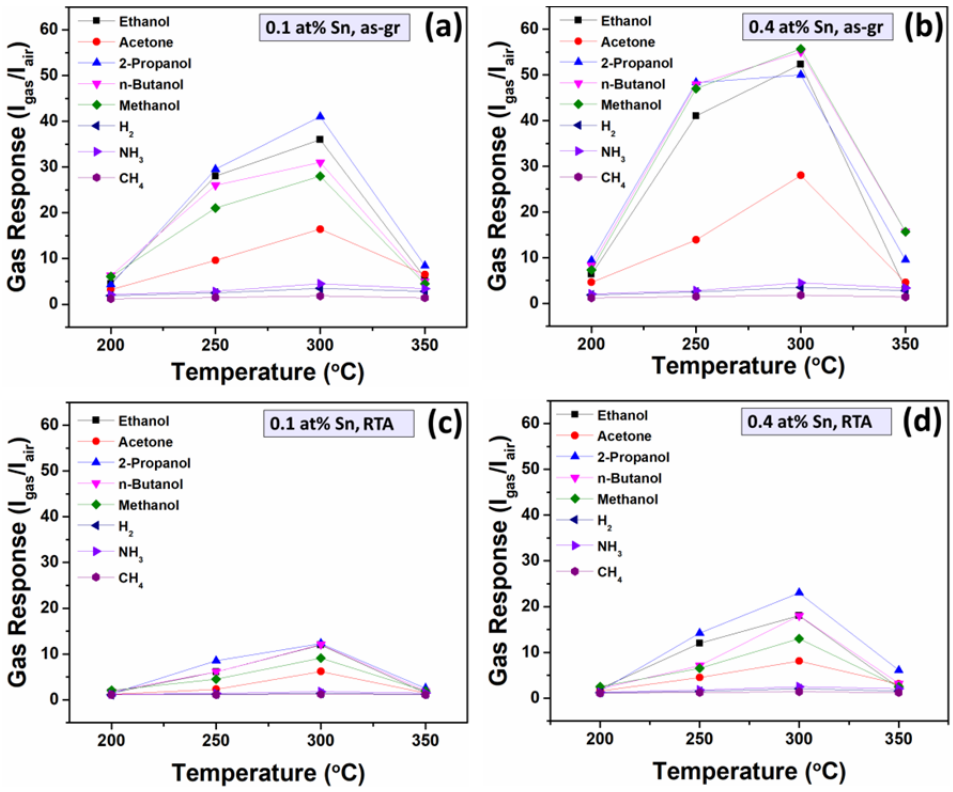

Figure 1. The gas response versus operating temperature for ZnO:Sn nanostructured films: (a) 0.1 at% Sn, as-grown; (b) 0.4 at% Sn, as-grown; (c) 0.1 at% Sn, RTA at 725 ºC; (d) 0.4 at% Sn, RTA at 725 ºC

of VOCs vapors (ethanol, acetone, 2-propanol, *n*-butanol and methanol) are 100 ppm, while concentrations of H_2, NH_3 and CH_4 are 1000 ppm. It can be seen, that the optimal operating temperature for both samples is 250 – 300 ºC. The highest gas response is observed for samples with higher content of Sn, i.e. 0.4 at% (see Figure 1b). However, for H_2, NH_3 and CH_4 no response higher than 5 is observed, which demonstrates high selectivity of ZnO:Sn nanostructured films to VOCs vapors. The values of gas response are also presented in Table 1.

Next, the influence of RTA treatment at 725 ºC for 60 s is investigated. Figure 1c and 1d show the gas response versus operating temperature for RTA treated samples with 0.1 and 0.4 at% Sn, respectively. For both cases, the considerable decrease in response is observed. The obtained results are also presented in Table 1.

Table 1

The gas response of ZnO:Sn samples to 100 ppm of VOCs vapors and 1000 ppm of H_2, NH_3 and CH_4 gas

ZnO:Sn sample	Temperature (ºC)	Gas Response							
		Ethanol	Acetone	2-Propanol	*n*-Butanol	Methanol	H_2	NH_3	CH_4
0.1 at% Sn, as-grown	200	4.5	3.2	4.3	6.3	6.1	1.9	2.1	1.2
	250	28	9.6	29.5	26	21	2.5	2.8	1.5
	300	36	16.4	4.1	31	28	3.5	4.5	1.8
	350	5.8	6.5	8.4	4.9	4.5	2.8	3.4	1.4
0.1 at% Sn, RTA at 725 ºC	200	1.5	1.2	1.35	1.8	2.1	1.1	1.2	1.1
	250	6.1	2.3	8.5	6.1	4.5	1.2	1.4	1.1
	300	12	6.2	12.3	12.1	9.1	1.4	1.8	1.2
	350	1.5	1.5	2.5	1.9	1.95	1.2	1.5	1.1
0.4 at% Sn, as-grown	200	6.4	4.6	9.4	8.3	7.3	1.9	2.1	1.2
	250	41	13.9	48.3	47.9	47	2.5	2.8	1.5
	300	52.2	28	50	55	55.7	3.5	4.5	1.8
	350	3.1	4.6	9.5	15.7	15.7	2.8	3.4	1.4
0.4 at% Sn, RTA at 725 ºC	200	2.1	1.6	1.6	2.1	2.5	1.2	1.3	1.1
	250	12	4.5	14.2	7.1	6.5	1.5	1.8	1.2
	300	18	8.1	23	18	13	2.1	2.5	1.4
	350	2.3	3.1	6.1	3.2	2.5	1.6	2.1	1.2

The dynamic response to 100 ppm of VOCs for ZnO:Sn nanostructured films with 0.4 at% Sn at 250 ºC and 300 ºC has been investigated. As can be observed, at both temperatures, which is the optimal regime for higher response to VOCs (see Figure 2), the recovery of signal is relatively fast and completely drops to the initial baseline, which is very important for practical applications. The response and recovery times are usually defined as the time to reach or to recover 90% of the total response, respectively. The response time is varying in a range of 100 – 150 s at 250 ºC and 50 – 120 s at 300 ºC, while the recovery times for all samples are 15 – 25 s at 250 ºC and 5 – 15 s at 300 ºC, respectively.

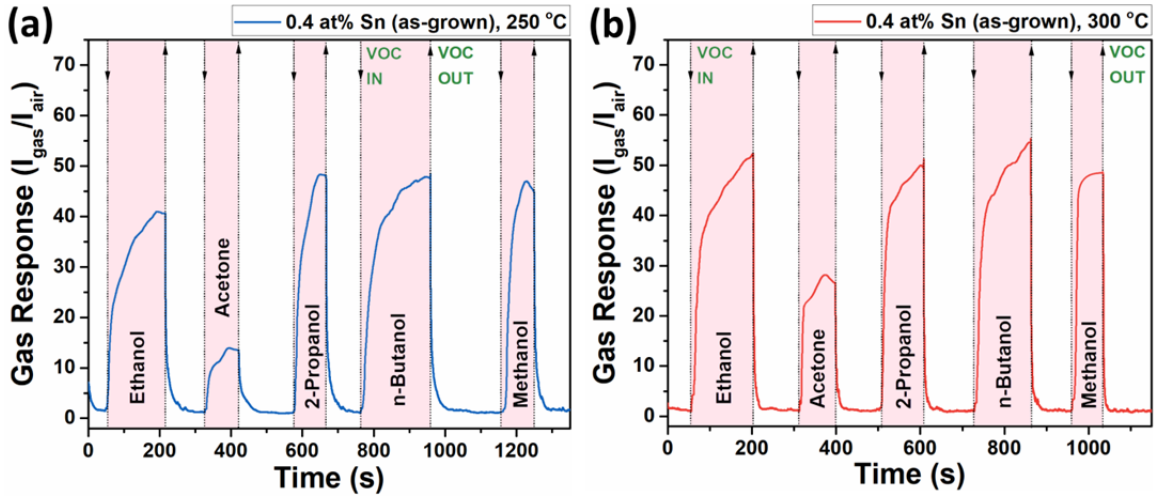

Figure 2. The dynamic gas response to 100 ppm of VOCs vapors for samples with 0.4 at% Sn: (a) at 250 °C and (b) at 300 °C

Based on gas sensing investigations of ZnO:Sn nanostructured films the following conclusions can be made: (i) doping of ZnO with Sn leads to high selectivity to VOCs vapors; (ii) the higher content of Sn, i.e. 0.4 at% for this study is more favorable for higher gas response to VOCs vapors; (iii) RTA treatment leads to decrease in gas response.

The gas response of ZnO nanostructured films composed of partially interconnected grains was already illustrated and discussed in detail in our previous work [18], and was based on the modulation of potential barriers height ($q\Delta V_s$) formed between grains due to the adsorption of oxygen species at the surface of ZnO grains [19]:

$$2O^-_{(ads)} + 2H_2 \rightarrow 2H_2O + 2e^- \quad (1)$$

In this case, the gas response of sensors can be expressed as follow:

$$S = \frac{I_{gas}}{I_{air}} \approx \exp\left(-\frac{q\Delta V_s}{2kT}\right) \quad (2)$$

where k is the Boltzmann constant and T is the absolute temperature. During exposure of the sensor to VOCs vapors, the VOC molecules are oxidized by the following reactions [20]:

$$CH_3COCH_3(acetone) + 8O^- \leftrightarrow 3CO_2 + 3H_2O + 8e^- \quad (2)$$

$$C_2H_5OH(ethanol) + 6O^- \leftrightarrow 2CO_2 + 3H_2O + 6e^- \quad (3)$$

$$CH_3OH(methanol) + O^- \leftrightarrow HCHO + H_2O + e^- \quad (4)$$

$$C_3H_7OH(2-propanol) + O^- \rightarrow (CH_3)_2CO(acetone) + H_2O + e^- \quad (5)$$

$$C_4H_9OH(n-but) + 12O^- \rightarrow 4CO_2 + 5H_2O + 24e^- \quad (6)$$

In our case, the increase in gas response for samples with higher content of Sn can be explained as follow. Previous optical investigations, namely photoluminescence of ZnO:Sn nanostructured films demonstrated that increase in Sn content leads to a higher amount of defects such as oxygen vacancies (V_O), interstitial oxygen (O_i) and interstitial zinc (Zn_i) [14]. It is well known and experimentally demonstrated that V_O-related defects can significantly enhance the gas sensitivity due to more adsorbed oxygen species [21]. This, will lead to a higher coverage with oxygen species and higher modulation of potential barriers height, i.e. higher gas response (see Eq. (2)) [22, 23]. This also explains very well the decrease in gas response for RTA treated samples, independent on Sn content. The RTA treatment is known to reduce the surface defects of ZnO micro- and nanostructures [24], which was also demonstrated for these ZnO:Sn nanostructured films in previous work [14], and therefore reduces the gas response of these samples. Another reason for decrease in response is the increase in grains size. Figure 3 shows the distribution of ZnO:Sn grains diameter for as-grown and RTA treated samples with 0.4 at% Sn. As can be observed, the as-grown films have the grains diameter in range of 200 – 400 nm, while RTA treatment increases the diameter of grains to 250 – 600 nm.

The grains size is also an important parameter for gas sensing properties of nanostructured films [25]. It is demonstrated that the smaller the grain size, the higher its gas response will be [25, 26]. Decrease in grains size leads to an increased surface activity of ZnO and the formation of more potential barriers between grains, which as was discussed, are very important factor for the increase in the performances of gas sensors based on micro- and nanostructures of metal oxides [25, 26].

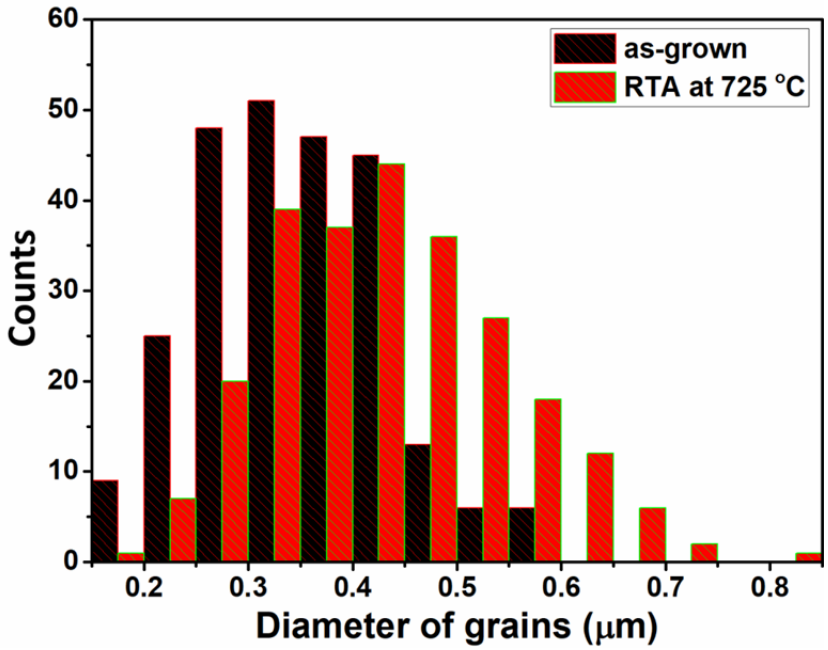

Figure 3. The grain diameter distribution for as-grown and RTA treated ZnO:Sn nanostructured films

Conclusions

The gas sensing properties of Sn-doped ZnO nanostructured films synthesized via an SCS approach are investigated in detail. The two relatively low contents of Sn in samples are used, namely the 0.1 and 0.4 at% Sn. It is found that the ZnO:Sn samples are highly selective to VOCs vapors as compared to other gases such as H_2, CH_4 and NH_3, which makes

them very attractive as VOCs sensors for the indoor air quality monitoring. The higher content of Sn is found to be more favorable for high gas response. The optimal operating temperature is 250 – 300 ºC. The grains diameter and defects density is found to be crucial for determination of gas sensitivity. The obtained results demonstrate that smaller grains and higher density of V_O defect, as in the case of ZnO:Sn as-grown films, are more favorable for fabrication of high-performance VOCs sensors.

Acknowledgments. Author would like to express sincere gratitude to prof. univ., dr. hab. Lupan Oleg, Ph.D. Thesis supervisor, for support, encouragement and guidance during doctoral studies at the Technical University of Moldova and for fruitful discussions. This research was partly supported by the STCU and ASM within the Grant 6229.

References

1. Tasaltin, C., Basarir, F. Preparation of flexible VOC sensor based on carbon nanotubes and gold nanoparticles. In: *Sensors and Actuators B: Chemical*, 2014, 194 pp. 173-9.
2. Matsuguchi, M., Uno, T. Molecular imprinting strategy for solvent molecules and its application for QCM-based VOC vapor sensing. In: *Sensors and Actuators B: Chemical*, 2006, 113 (1), pp. 94-9.
3. Zhu, B.L. Xie, Cs., Wang, W.Y., Huang, K.J., Hu, J.H. Improvement in gas sensitivity of ZnO thick film to volatile organic compounds (VOCs) by adding TiO_2. In: *Materials Letters*, 2004, 58 (5), pp. 624-9.
4. Srivastava, A.K. Detection of volatile organic compounds (VOCs) using SnO_2 gas-sensor array and artificial neural network. In: *Sensors and Actuators B: Chemical*, 2003, 96 (1), pp. 24-37.
5. Meng, F., Hou, N., Ge, S., Sun, B., Jin, Z., Shen, W., Kong, L., Guo, Z., Sun, Y., Wu, H., Wang, C., Li, M. Flower-like hierarchical structures consisting of porous single-crystalline ZnO nanosheets and their gas sensing properties to volatile organic compounds (VOCs). In: *Journal of Alloys and Compounds*, 2015, 626 pp. 124-30.
6. Li, W., Wu, X., Han, N., Chen, J., Qian, X., Deng, Y., Tang, W., Chen, Y. MOF-derived hierarchical hollow ZnO nanocages with enhanced low-concentration VOCs gas-sensing performance. In: *Sensors and Actuators B: Chemical*, 2016, 225 pp. 158-66.
7. Al-Hardan, N.H., Abdullah, M.J., Abdul Aziz, A., Ahmad, H., Low, L.Y. ZnO thin films for VOC sensing applications. In: *Vacuum*, 2010, 85 (1), pp. 101-6.
8. Liu, L., Zhang, D., Zhang, Q., CHEN, X., Xu, G., Lu, Y., Liu, Q. Smartphone-based sensing system using ZnO and graphene modified electrodes for VOCs detection. In: *Biosensors and Bioelectronics*, 2017, 93 pp. 94-101.
9. Cao, W., Duan, Y. Current Status of Methods and Techniques for Breath Analysis. In: *Critical Reviews in Analytical Chemistry*, 2007, 37 (1), pp. 3-13.
10. Miekisch, W., Schubert, J.K., Noeldge-Schomburg, G.F.E. Diagnostic potential of breath analysis—focus on volatile organic compounds. In: *Clinica Chimica Acta*, 2004, 347 (1), pp. 25-39.
11. Nakhleh, M.K., Amal, H., Jeries, R. Diagnosis and Classification of 17 Diseases from 1404 Subjects via Pattern Analysis of Exhaled Molecules. In: *ACS Nano*, 2017, 11 (1), pp. 112-25.
12. Righettoni, M., Tricoli, A., Pratsinis, S.E. Si:WO_3 Sensors for Highly Selective Detection of Acetone for Easy Diagnosis of Diabetes by Breath Analysis. In: *Analytical Chemistry*, 2010, 82 (9), pp. 3581-7.
13. Kim, S-J., Choi, S-J., Jang, J-S., Cho, H-J., Kim, I-D. Innovative Nanosensor for Disease Diagnosis. In: *Accounts of Chemical Research*, 2017, 50 (7), pp. 1587-96.
14. Postica, V., Hoppe, M., Gröttrup, J., Hayes, P., Röbisch, V., Smazna, D., Adelung, R., Viana, B., Aschehoug, P., Pauporté, T., Lupan, O. Morphology dependent UV photoresponse of Sn-doped ZnO microstructures. In: *Solid State Sciences*, 2017, 71 pp. 75-86.
15. Cretu, V., Postica, V., Mishra, A.K., Hoppe, M., Tiginyanu, I., Mishra, Y.K., Chow, L., De Leeuw, N. H.; Adelung, R., Lupan, O. Synthesis, characterization and DFT studies of zinc-doped copper oxide nanocrystals for gas sensing applications. In: *Journal of Materials Chemistry A*, 2016, 4 (17), pp. 6527-39.
16. Lupan, O., Cretu, V., Postica, V., Ababii, N., Polonskyi, O., Kaidas, V., Schütt, F., Mishra, Y. K., Monaico, E., Tiginyanu, I., Sontea, V., Strunskus, T., Faupel, F., Adelung, R. Enhanced ethanol vapour sensing performances of copper oxide nanocrystals with mixed phases. In: *Sensors and Actuators B: Chemical*, 2016, 224 pp. 434-48.

17. Lupan, O., Postica, V., Mecklenburg, M., Schulte, K., Mishra, Y.K., Fiedler, B., Adelung, R. Low powered, tunable and ultra-light aerographite sensor for climate relevant gas monitoring. In: *Journal of Materials Chemistry A*, 2016, 4 (42), pp. 16723-30.
18. Postica, V., Hölken, I., Schneider, V., Kaidas, V., Polonskyi, O., Cretu, V., Tiginyanu, I., Faupel, F., Adelung, R., Lupan, O. Multifunctional device based on ZnO:Fe nanostructured films with enhanced UV and ultra-fast ethanol vapour sensing. In: *Materials Science in Semiconductor Processing*, 2016, 49 pp. 20-33.
19. Hübner, M., Simion, C.E., Tomescu-Stănoiu, A., Pokhrel, S., Bârsan, N., Weimar, U. Influence of humidity on CO sensing with p-type CuO thick film gas sensors. In: *Sensors and Actuators B: Chemical*, 2011, 153 (2), pp. 347-53.
20. Feng, Z., Ma, Y., Natarajan, V., Zhao, Q., Ma, X., Zhan, J. In-situ generation of highly dispersed Au nanoparticles on porous ZnO nanoplates via ion exchange from hydrozincite for VOCs gas sensing. In: *Sensors and Actuators B: Chemical*, 2018, 255 pp. 884-90.
21. Ahn, M.W., Park, K.S., Heo, J.H., Park, J.G., Kim, D.W., Choi, K.J., Lee, J.H., Hong, S.H. Gas sensing properties of defect-controlled ZnO-nanowire gas sensor. In: *Applied Physics Letters*, 2008, 93 (26), pp. 263103.
22. Zhang, Y., Xu, J., Xiang, Q., Li, H., Pan, Q., Xu, P. Brush-Like Hierarchical ZnO Nanostructures: Synthesis, Photoluminescence and Gas Sensor Properties. In: *The Journal of Physical Chemistry C*, 2009, 113 (9), pp. 3430-5.
23. Chen, M., Wang, Z., Han, D., Gu, F., Guo, G. Porous ZnO Polygonal Nanoflakes: Synthesis, Use in High-Sensitivity NO2 Gas Sensor, and Proposed Mechanism of Gas Sensing. In: *The Journal of Physical Chemistry C*, 2011, 115 (26), pp. 12763-73.
24. Shishiyanu, S.T., Lupan, O.I., Monaico, E., Ursaki, V., Shishiyanu, T., Tiginyanu, I.M. Photoluminescence of chemical bath deposited ZnO:Al films treated by rapid thermal annealing. In: *Thin Solid Films*, 2005, 488 (1),
pp. 15-9.
25. Xu, J., Pan, Q., Shun, Y.A., Tian, Z. Grain size control and gas sensing properties of ZnO gas sensor. In: *Sensors and Actuators B: Chemical*, 2000, 66 (1), pp. 277-279.
26. Trinh, T.T., Tu, N.H., Le, H.H., Ryu, K.Y., Le, K.B., Pillai, K., Yi, J. Improving the ethanol sensing of ZnO nano-particle thin films—The correlation between the grain size and the sensing mechanism. In: *Sensors and Actuators B: Chemical*, 2011, 152 (1), pp. 73-81.