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SnO₂ ve Zn_{0.50}Sn_{0.50}O sensörlerinin düşük NO gaz konsantrasyonu algılama özellikleri

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Low Concentration NO Gas Detection of SnO₂ and Zn_{0.50}Sn_{0.50}O Sensors

Highlights

- ❖ The sensitivity and given response to 50 ppb NO gas
- ❖ The response to low temperature (105 °C)

Graphical Abstract

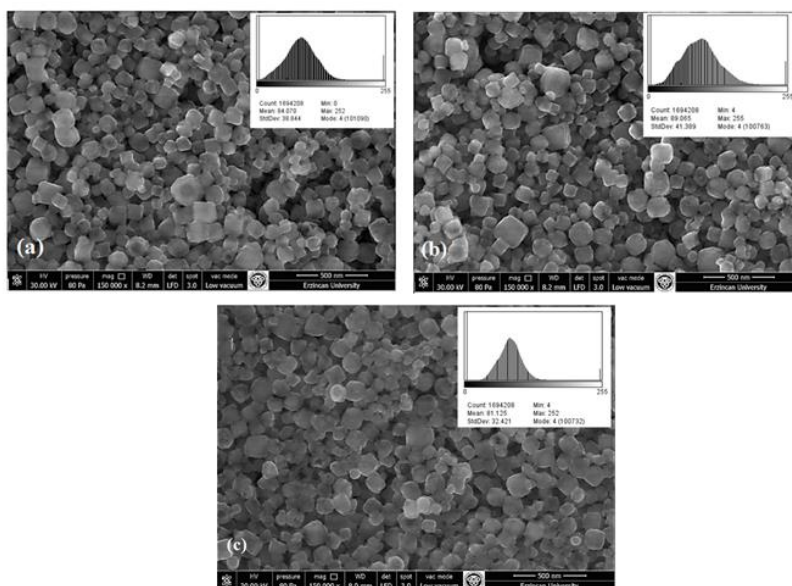


Figure. SEM Analysis (Zn_{0.50}Sn_{0.50}O)

Aim

In this study, the gas sensing properties of SnO₂ and Zn_{0.50}Sn_{0.50}O samples produced by Succession Ionic Layer Adsorption and Reaction (SILAR) method with different SILAR cycles against NO gas were investigated.

Design & Methodology

In this study, sensors were produced with the cheap, practical and fabricated Succession Ionic Layer Adsorption and Reaction (SILAR) method.

Originality

The sensors can be seen to show high responses to a relatively low NO gas concentration, such as 50 ppb.

Findings

For 50 ppb NO gas concentration, 3.01, 3.74% and 4.16% sensitivities were obtained for 20, 30 and 40 cycles, respectively, while for 25 ppm 18%, 20% and 34% sensitivities were obtained, respectively.

Conclusion

The results show that Zn doping greatly increases the response sensors. Also, Zn doping introduces some defects in the sensors, and these defects make the structure unstable and more possible to react with gas molecules.

Declaration of Ethical Standards

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

SnO₂ ve Zn_{0.50}Sn_{0.50}O Sensörlerinin Düşük NO Gaz Konsantrasyonu Algılama Özellikleri

Araştırma Makalesi / Research Article

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ÖZ

Bu çalışmada, SnO₂ ve Zn_{0.50}Sn_{0.50}O örnekleri Ardışık İyonik Katman Adsorpsiyon ve Reaksiyon yöntemiyle 3 farklı döngüde üretildi ve NO gaz algılama özellikleri incelendi. Üretilen numunenin farklı sıcaklıklarda (35°C-135°C) ve farklı gaz konsantrasyonlarında (50 ppb-25 ppm) elektriksel karakterizasyonu yapıldı. Çalışma sıcaklığı 105 °C olarak bulundu. Sensörler 50 ppb NO gazına karşı kabul edilebilir düzeyde duyarlılık sergiledi. Zn_{0.50}Sn_{0.50}O sensörü, 105 °C çalışma sıcaklığında SnO₂ sensörüne kıyasla daha yüksek algılama performansı gösterdi. 20, 30 ve 40 döngü SnO₂ sensörlerinin 50 ppb NO gaz konsantrasyonu için gösterdiği duyarlılıklar sırasıyla % 1.74,% 2.15 ve % 3.37 olarak hesaplandı. Öte yandan, Zn_{0.50}Sn_{0.50}O sensörlerinin 50 ppb NO gaz konsantrasyonu için gösterdiği duyarlılıklar sırasıyla % 3.01,% 3.74 ve % 4.16 olarak elde edilmiştir. Ölçüm sonuçları, numunelerin gaz algılama özelliklerinin katılma ve üretim döngüsüne bağlı olarak değiştiğini gösterdi.

Anahtar Kelimeler: Gaz algılama, SILAR metot, NO gaz.

Low Concentration NO Gas Detection Of SnO₂ And Zn_{0.50}Sn_{0.50}O Sensors

ABSTRACT

In this study, the gas sensing properties of SnO₂ and Zn_{0.50}Sn_{0.50}O samples produced by Succession Ionic Layer Adsorption and Reaction (SILAR) method with different SILAR cycles against NO gas were investigated. Electrical characterization of the produced sample at different temperatures (35 °C-135 °C) and different gas concentrations (50 ppb-25 ppm) were performed. The working temperature was found at 105 °C. The sensors were proved to have acceptable responses towards 50 ppb NO gas. Zn_{0.50}Sn_{0.50}O sensor exhibited improved sensing performance at working temperature of 105 °C compared to SnO₂ sensor.. The responses of SnO₂ sensors for the 50 ppb NO gas concentration, sensitivities of 1.74%, 2.15% and 3.37% were obtained for 20, 30 and 40 cycles, respectively. On the other hand, the responses of Zn_{0.50}Sn_{0.50}O sensors for the 50 ppb NO gas concentration sensitivities of 3.01%, 3.74% and 4.16% were obtained for 20, 30 and 40 cycles, respectively. The measurement results showed that the sensitivity of the sensors changed depending on the doping and producing cycles.

Keywords: Gas sensing, SILAR method, NO gas.

1. INTRODUCTION

The monitoring and environmental control of pollutants in the atmosphere has increased recently due to their harmful effects on human health and global warming [1]. Among various pollutants, nitric oxide is color less, readily diffusible, highly reactive and chemically unstable free radical gas [2]. Nitric oxide (NO) as a biological mediator plays an important role in a variety of biological processes and is a fundamental component in the fields of biochemistry, physiology, immunology and neuroscience [3]. It is well-known today that NO acts in the human body as a signalling molecule of key

importance in the nervous system as a weapon against infections, as a regulator of blood pressure and as a gatekeeper of blood flow to different organs. It is also established that NO concentration in the exhaled air increases in inflammatory conditions of the airways. Especially, sensitive and selective detection of NO in human breath plays an important role in the diagnosis of asthma. However, obtaining a reliable response to ppb levels of NO is still a great challenge [4].

Designing better sensors which are faster, more sensitive and selective is a continuing need to satisfy the standard in various applications [5]. The development of gas sensors is currently being carried out intensively since environmental pollution and security in the world and

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domestic ambient atmospheres represent acute problems with a high social impact [6].

Among them, Metal-oxide semiconductors (MOS) gas sensors which monitor and detect the explosive, inflammable or toxic gases in the environment are investigated, extensively. Development of gas sensors with high surface to volume ratio, porous surface, different production methods, different doping materials, the use of different metal oxide surfaces are shown positive signs for the detection of pollutant gases. In as much as formation of (i) mixture in atomic level, (ii) dopant materials and (iii) porosity- surface area with desirable size and surface morphology are significant issues about performance of devices, especially, in fabrication of gas sensors [7].

Among them, SnO₂ based sensors are the most preferred materials for gas sensor applications due to their ability to easily detect various gases which cause environmental pollution even at low concentrations and have the ability to respond quickly and have high gas sensitivity [8]. Mixing of suitable dopant in crystal lattice modify the defect chemistry and microstructure of the system which further results in a change of its properties [9]. The addition of cationic dopants produces high densification and reduced particle size [10]. Researchers have shown that the doping increased the sensor response of MOS materials. Guan et al. have reported that doping the SnO₂ sensors with Zn exhibited the high responses which was about 3.2 times higher compared to the pure SnO₂ [11]. Gupta et al. have shown that Zn-doping has been found to increase the sensitivity of oxygen than the pure SnO₂ [12]. Singh et al. have studied that the doping concentration of zinc (x=0.20%) exhibited the maximum response within the concentration of 100 ppm of each gases compared to the SnO₂ [13].

The gas sensitivity, gas selectivity, the ability to respond in the gas medium and the working temperature range of the sensor are generally the most critical features of the gas sensors. These critical sensor features need to be checked for the production of high-performance gas sensors. For this, the material structure-property relationship should be discussed and it should be decided which material properties affect these critical gas sensor properties. So, the selection of economic and effective production techniques is required.

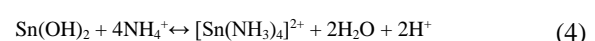
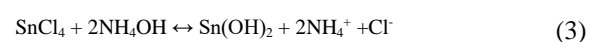
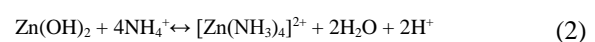
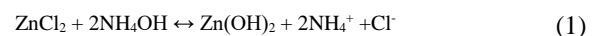
One of the most economic and effective production technique for producing thin films is Succession Ionic Layer Adsorption and Reaction (SILAR) method. SILAR is an aqueous solution method that involves sequential reactions at the substrate-solution interface. It is a simple method that allows thin films to be formed by immersing the base material in aqueous solutions containing ions of each species in a certain order and precipitating on the base material. As it is a low temperature process, oxidation and corrosion of the base material is prevented. From this point of view, SILAR method includes several advantages such as production of well-defined oxides with excellent homogeneity and incorporation of dopant

materials with extreme purity for fabrication of gas sensor components [14]. The SILAR method has many advantages: (i) to add the film in any proportion to any element, it is enough to include it only in certain forms of the cationic or anionic solution, and this is a very simple way. (ii) SILAR does not require a high-quality target or substrate, or vacuum at any stage, which provides great convenience and low cost compared to other thin-film growth techniques. (iii) The thickness of the thin film to be produced can be easily controlled by varying the SILAR cycle number. (iv) with room temperature operations, the film can be enlarged [15]. In addition, it is useful for deposition in a cheap, simple and wide area compared to other methods. In present work, the SnO₂ and Zn_{0.50}Sn_{0.50}O thin films have been produced by SILAR method and NO gas sensing properties have been studied.

2. EXPERIMENTAL SETUP

The SnO₂ and Zn_{0.50}Sn_{0.50}O samples were produced by SILAR method. Before producing the samples, the metal contacts for the samples were generated using the thermal evaporation system on the glass substrates. For interdigital contact, high purity (99.999%) gold (Au) was placed on the tungsten filament in the thermal evaporation system. SILAR is an aqueous solution technique involving a series of sequential reactions between the substrate and the solution, in which the material used as the substrate is immersed in aqueous solutions containing ions of each type of compound semiconductor to be grown [15].

When the solutions of ZnCl₂, SnCl₄ and NH₃ are mixed, reactions occur and a complex of [Zn(NH₃)₄]²⁺ and ([Sn(NH₃)₄]⁴⁺) (pH≅10) is formed. Substrate material was suspended in [Zn(NH₃)₄]²⁺ and ([Sn(NH₃)₄]⁴⁺) solution for 20 seconds and the thin film layer was coated on the substrate (given in Eqs. (1)- (4)). The substrate was removed from the solution and waited in distilled water at 90 °C for 7 seconds. Substrates were kept in air for 60 seconds. Thereafter, it was left in distilled water at room temperature for 30 seconds. A SILAR cycle was thus completed and Zn_{1-x}Sn_xO films were grown on substrates. ('x' is defined as doping ratio for producing samples). Possible reactions were given as follows;



Throughout our previous works, samples were produced in various cycles and SILAR cycles were optimized [14-17]. It has been determined in our previous studies that the most suitable cycles are 20, 30 and 40. According to our previous studies; the samples were prepared for 20, 30 and 40 SILAR cycles.

The thickness of thin films was measured using a stylus ellipsometer system (J. A. Woolam Co, Inc., V-VASE). The thickness of Zn_{0.50}Sn_{0.50}O films were measured 70 nm, 79 nm, 89 nm for 20, 30 and 40 cycles and SnO₂ were measured 75 nm, 84 nm, 92 nm for 20, 30 and 40 cycle, respectively. For structural, morphological, compositional and optical studies, the Panalytical empyrean X-Ray Diffractometer (using Cu K α $\lambda=1.5405\text{\AA}$ radiation) and the FEI Quanta FEG 450 model Scanning Electron Microscope (SEM) were used, respectively. The gas-sensing performance of the sensors has been carried out a computer-controlled measurement system [14-15].

The gas sensor was connected into the sensing system according to the test circuit and the changes of sensor resistance were recorded in real time [16]. The gas sensor system includes computer controlled mass flow controllers (MKS Series), A Lakeshore 325 temperature controller, Keithley 2400 sourcemeter, the data was collected in real time using the data acquisition hardware and software of the same company. Figure 1 shows the gas sensing measurement system.

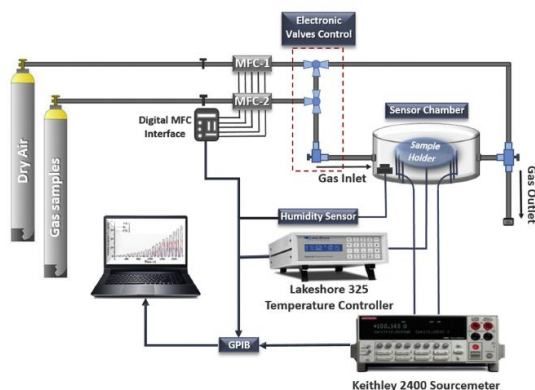


Figure 1. The gas sensing measurement system [17].

3. RESULTS AND DISCUSSIONS

Fig. 2 shows the XRD patterns of thin films. As seen in Fig. 2, all the thin films have polycrystalline nature and well-defined peaks belonging to ZnO and SnO₂. The diffractogram of the pure ZnO reveals that all the peaks are in good agreement with the JCPDS data belonging to hexagonal ZnO structure (Card No. 36-1451). It was determined that the quality of the ZnO thin films and the crystallization were influenced by rinsing period. The peaks belonging to ZnO thin film decreased and began to disappear with increasing Sn concentration [17]. The intensities of the characteristic peaks of ZnO the diffractogram of the pure SnO₂ reveals that all the peaks are in good agreement with the JCPDS data belonging to tetragonal phase. (JPCDS Card No:41-1445) [17]. The films with compositions in the range of $0 < x < 1$ have both hexagonal wurtzite and tetragonal crystal phases. The crystal quality of the thin films deteriorated with increasing Sn concentration [18]. This degradation may be connected to the changing in the atomic environment due to the external doping (Sn) of ZnO thin film. Besides,

Sn doping concentrations were changed the peak positions smoothly bigger refraction angles. It has been related to the unit cell size changes in the structures with the substitution of Sn⁴⁺ for Zn²⁺, because the ionic radius of Zn²⁺ (0.74 Å) and Sn⁴⁺ (0.69 Å) are different values. Also, the Zn(OH)₂ phase was not detected by XRD. This suggests that Zn(OH)₂ might exist inside the thin film as an amorphous phase.

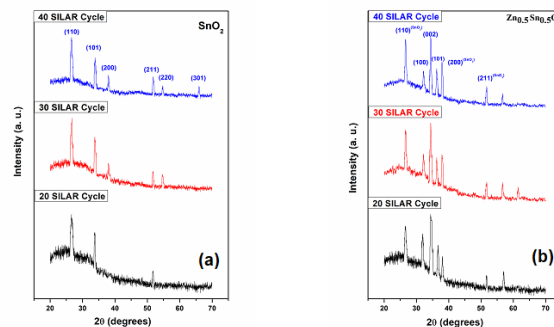


Figure 2. The XRD analysis of SnO₂ (a) and Zn_{0.50}Sn_{0.50}O (b) samples

Figure 3 depicts the SEM images of SnO₂ samples, 20 cycle (a), 30 cycle (b) and 40 cycle (c). It was observed that a smooth film structure homogeneously spreading to the surface was observed for all cycles. Figure 4 depicts the SEM images of Zn_{0.50}Sn_{0.50}O samples, 20 cycle (a), 30 cycle (b) and 40 cycle (c). For all cycles, cubic-like structures were observed in Zn_{0.50}Sn_{0.50}O samples with dopant effect [19]. 40 cycle Zn_{0.50}Sn_{0.50}O sample has more porous sphere and localized cubic-like structures compared to other ones. It can be also seen on the SEM analysis; according to particle distribution analysis; Figure 3 (a); 76.886 , Figure 3 (b); 77.857 , Figure 3 (c); 68.654 and Figure 4 (a); 84.070 , Figure 4 (b); 89.065 , Figure 4 (c); 81.125 values are calculated with image j programme.

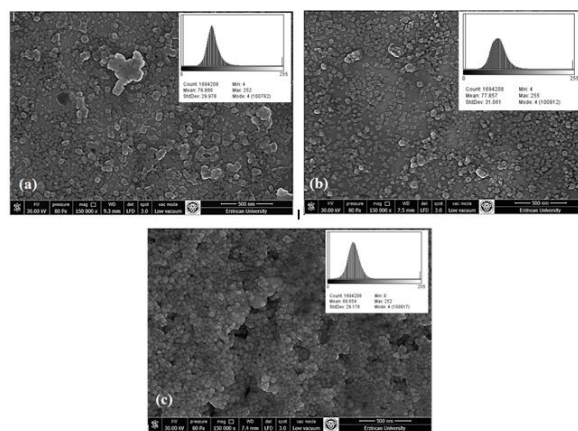


Figure 3. The SEM images of SnO₂ samples, 20 cycle (a), 30 cycle (b) and 40 cycle (c)

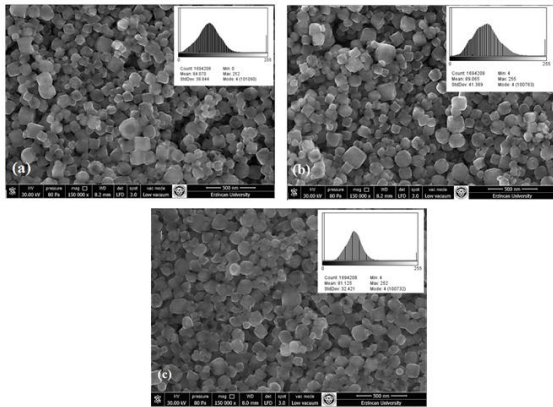


Figure 4. The SEM images of $Zn_{0.50}Sn_{0.50}O$ samples, 20 cycle (a), 30 cycle (b) and 40 cycle (c)

The working temperature of a gas sensor is one of the main factors for the gas detection of the sensors. Increasing temperature is necessary to acceleration surface reactions and a considerable sensitivity. However, high temperatures can deteriorate the material structure and affect the life of the sensor. For this reason, it is necessary to determine the elevated working temperatures for the sensor materials. Figure 5 shows the the responses of SnO_2 and $Zn_{0.50}Sn_{0.50}O$ samples for 20,30 and 40 cycles as a function of working temperature for 25 ppm NO gas. As seen in the graphs, there was an increase in the responses as the temperature increased. The working temperature was found at 105 °C. After this temperature, the responses began to decrease. Actually, the temperature (thermal energy) at which the gas response is maximum is necessary to arouse the material in reaction. However, the adsorbed oxygen began to desorb from the sensing surface and with this the response decreased at higher working temperature [20]. The increase in film thickness (SILAR cycle) can be attributed to the improvement in crystal structure, morphological changes, the decrease in the forbidden energy range, changes in particle size and atomic distances. In addition, some defect levels that occur during the amplification process are combined with the conductivity band as the film thickness increases, thus reducing the forbidden energy range.

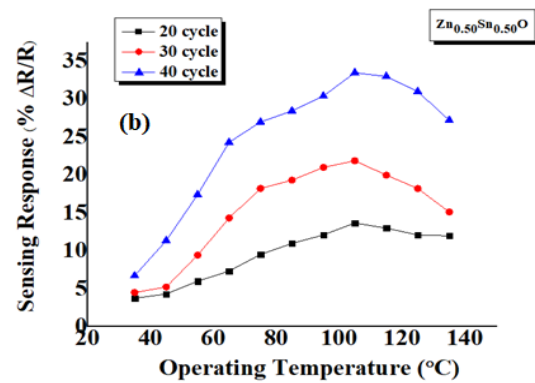
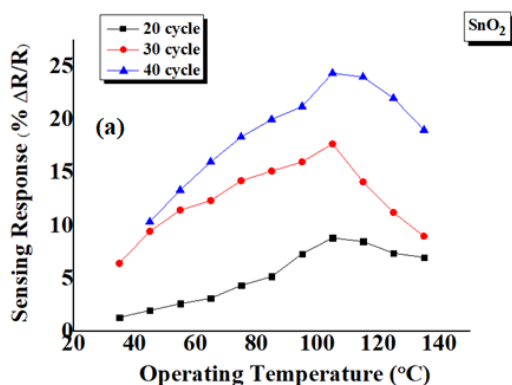


Figure 5. The responses of SnO_2 (a) and $Zn_{0.50}Sn_{0.50}O$ (b) samples for 20,30 and 40 cycles as a function of working temperature for 25 ppm NO gas concentrations

Figure 6 shows the responses of SnO_2 and $Zn_{0.50}Sn_{0.50}O$ samples as a function of gas concentrations from 50 ppb to 25 ppm at 105°C. As seen from the fig 6 (a), (b) and (c) the response of 40 cycle of SnO_2 was obtained 24%, while 20 and 30 cycles were obtained 9% and 18% , respectively. Also, it is determined that the sensors produced can select each gas concentration separately. For the 50 ppb NO gas concentration, sensitivities of 1.74%, 2.15% and 3.37% were obtained for 20, 30 and 40 cycles, respectively. As shown in the graph, NO gas was adsorbed on the surface and caused an increase in sensitivity. When exposed to dry air, the response began to baseline value. Figure 6 (d), (e) and (f), the response of 25 ppm NO gas for $Zn_{0.50}Sn_{0.50}O$ sensors was obtained 18%, 20% and 34%, were obtained for 20,30 and 40 cycles, respectively. It can be noticed that the samples exhibited high responses to very-low NO gas concentration (50 ppb). For the 50 ppb NO gas concentration, sensitivities of 3.01%, 3.74% and 4.16% were obtained for 20, 30 and 40 cycles, respectively. The above results show that Zn doping greatly increases the response sensors. The adsorption and desorption of Zn atoms with O_2 gases are more quickly than that of Sn atoms. Also, Zn doping introduces some defects in the sensors, and these defects make the structure unstable and more possible to react with gas molecules [21]. In addition the working temperature of the sensors, it was reported in the literature that the thickness of the produced sensors had an effect on the sensor parameters [22-24].

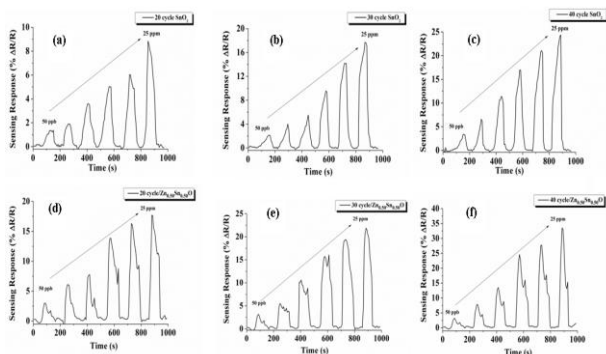


Figure 6. The responses of SnO₂ (a,b,c) and Zn_{0.50}Sn_{0.50}O (d,e,f) samples as a function of gas concentrations at 105 °C.

An ideal sensor should have a long life with high sensitivity, dynamic sensing range, selectivity stability and fast response time. All these parameters are used to characterize the sensor. However, all these parameters are not needed depending on the application areas and the usage areas of the sensors. Usually, some of these features are selected according to the application area and their improvement is emphasized. One of the main challenges to the metal-oxide gas sensors is high selectivity [1]. The results show that the sensors show different sensitivities to each gas concentration. Sensitivity increases as gas concentration increases. The sensor responses exhibit a linear increase.

Reproducibility is a crucial parameter for real-time gas sensors as it surely affects the sustainability and reliability of the sensor [25]. Hence, Fig 7. depicts the reproducibility of Zn_{0.50}Sn_{0.50}O (a) and SnO₂ (b) samples at 105 °C and they were displayed quite stable response after ten repeatable cycles (Fig. 7(a) and (b)). Therefore, Reproducibility tests clearly indicated that our sample is a quite stable with a little degradation.

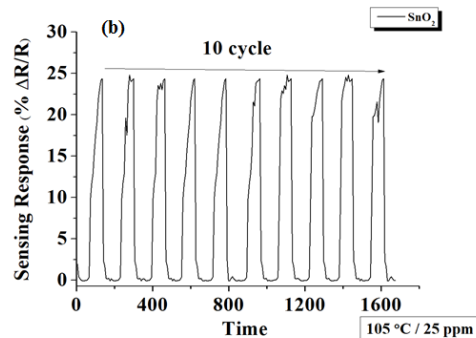
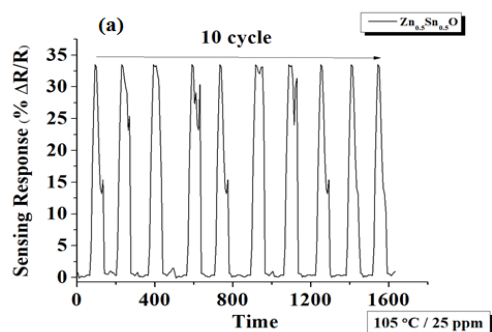


Figure 7. The reproducibility of Zn_{0.50}Sn_{0.50}O (a) and SnO₂ (b) samples at 105 °C.

The gas sensing mechanism consists of chemical reactions between chemically absorbed oxygen and target gases. As a result of these reactions, resistance change occurs in the sensor. Firstly, dry air exposed to the sensing surface and oxygen atoms adsorbed. The adsorbed oxygen species capture electrons from the conduction band, creating a depletion region in the samples. The electron transfer from the conduction band to the adsorbed oxygen species, decreasing the electron concentration of the surface [26]. After that, when the surface is exposed to NO gas, they react with the chemisorbed oxygen. Therefore, they capture the electrons from the sensing surface, enlarging the depletion region. A rapid increase in the resistance of the film with time up to stabilization was observed [25]. Possible reactions were given below as follow [27];



The chemical nature of oxygen bonding states which can act as active sites for NO molecule absorption, more active sites are available for NO gas. The adsorption of NO molecules will be promoted by the increased surface states, as results oxidizing molecules needs to be captured the electrons from surface. This enhanced ionosorption due to surface states result in a decreased activation energy. The obtained NO gas-sensing results were compared with the literature and tabulated in Table 1. It is confirmed that our samples has an acceptable response to very-low NO gas concentration.

Table 1. NO gas-sensing results comparison with previous reports

Materials	Producing Method	Gas Concentration	Sensing Response	Operating Temperature	References
ZnO nanorod thin films	Dip coating	70 ppm	90	300 °C	[28]
ZnGa ₂ O ₄ thin films	metalorganic chemical vapor deposition	6.25ppm	22.21	300 °C	[29]
Co ₃ O ₄ powder	mixed with an organic dispersant for obtaining a paste	1 ppm	1.2	200 °C	[30]
WO ₃ nanoparticles	an ICP-assisted hot wire system	350 ppb	15.93	150 °C	[31]
ZnO/Al ₂ O ₃ TiO ₂ /ZnO film /Al ₂ O ₃	screen-printing	10 ppm	50 / 150	320 °C	[32]
In ₂ O ₃ -ZnO	The chemical bath precipitation	10 ppm	8	100 °C	[33]
Zn _{0.50} Sn _{0.50} O /SnO ₂	SILAR	50 ppb	3.37	105 °C	In this work

With the doping of Zn, Zn atoms in substitutional Sn positions (Zn_{Sn}) favor the formation of V_O due to charge compensation [21]. It is probably because Zn atoms doped in SnO₂ sensor are more active than Sn atoms. The adsorption and desorption of Zn atoms with O₂ gases are more quickly than that of Sn atoms. Also, the surface area has an important influence on the gas sensing performance. Finally, Zn_{0.50}Sn_{0.50}O exhibited the higher responses compared to the pure SnO₂.

4. CONCLUSION

In this work, SnO₂ and Zn_{0.50}Sn_{0.50}O sensors have been grown by SILAR method. The working temperature was found at 105 °C. After this temperature, the responses began to decrease. The responses of SnO₂ and Zn_{0.50}Sn_{0.50}O samples as a function of gas concentrations from 50 ppb to 25 ppm at 105°C. The effect of doping material is shown that the responses improved with increasing doping concentrations. The effect of film thickness, as well as the sensing temperature, on the sensor characteristics of sensing films, were reported. The response of 40 cycle of SnO₂ was obtained 24%, while 20 and 30 cycles were obtained 9% and 18% , respectively. Also, it is determined that the sensors produced can select each gas concentration separately. For the 50 ppb NO gas concentration, sensitivities of 1.74%, 2.15% and 3.37% were obtained for 20, 30 and 40 cycles, respectively. The results show that Zn doping greatly increases the response sensors. The adsorption and desorption of Zn atoms with O₂ gases are more quickly than that of Sn atoms. Also, Zn doping introduces some defects in the sensors, and these defects make the structure unstable and more possible to react with gas molecules. Therefore, the response of 25 ppm NO gas for Zn_{0.50}Sn_{0.50}O sensors was obtained 18%, 20% and 34%, were obtained for 20,30 and 40 cycles, respectively. For the 50 ppb NO gas concentration, sensitivities of 3.01%, 3.74% and 4.16% were obtained for 20, 30 and 40 cycles, respectively. This improvement in response can be

explained by the doping of sensors. On the other hand, the substantial improvement in the response of sensors was attributed to the morphology of the sensors and the SILAR cycle. The film thickness has affected the responses of the sensors, increasing with increasing the film thicknesses. As a result, our study may ensure basic and new information for investigations on alternative gas sensor materials.

ACKNOWLEDGEMENT

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DECLARATION OF ETHICAL STANDARDS

The author(s) of this article declare that the materials and methods used in this study do not require ethical committee permission and/or legal-special permission.

REFERENCES

- [1] Onofre Y.J., Catto A.C., Bernardini S., Fiorido T., Aguir K., Longo E., Mastelaro V.R., da Silva L.F. and de Godoy M.P.F., "Highly selective ozone gas sensor based on nanocrystalline Zn_{0.95}Co_{0.05}O thin film obtained via spray pyrolysis technique", *Appl. Surf. Sci.*, 478: 347–354, (2019).
- [2] Shah C., Dixit R. and Anand A.K., "Nitric Oxide In Health And Diseases", *Global Journal of Medicine and Public Health*, GJMEDPH, 1(1): 73-78, (2012).
- [3] Khazan M. and Hdayati M., "The Role of Nitric Oxide in Health and Diseases", *Scimetr.* 3(1): 20987, (2015).
- [4] Rei Vilar M., El-Beghdadi J., Debontridder F., Naaman A. Arbel R., Ferraria A.M. and Botelho Do Rego A.M., "Development of nitric oxide sensor for asthma attack prevention", *Materials Science and Engineering C* 26: 253 – 259, (2006).
- [5] Gao H., Yu Q., Chen K., Sun P., Liu F., Yan X., Liu F., Lu G., Ultrasensitive gas sensor based on hollow tungsten trioxide-nickel oxide (WO₃-NiO) nanoflowers for fast and selective xylene detection, *J. Colloid Interface Sci.*, 535: 458-468, (2019).
- [6] Samerjai T., Channei D., Khanta C., Inyawilert K., Liewhiran C., Wisitsoraat A., Phokharatkul D. and Phanichphant S., "Flame-spray-made Zn-In-O alloyed nanoparticles for NO₂ gas sensing", *J Alloy. Compd.*, 680, 711-721, (2016).
- [7] Bai S., Tong W., Tian Y., Fu H., Zhao Y., Shu X., Luo R., Li D. and Chen A., "Facile synthesis of Pd-doped ZnSnO₃ hierarchical microspheres for enhancing sensing properties of formaldehyde", *J. Mater. Sci.*, 54(3): 2025–2036, (2019).

- [8] Karaduman I., Barin Ö., Yıldız D.E. and Acar S., "Atomik Tabaka Biriktirme Metodu ile Üretilen HfO₂ Tabanlı Sensörlerin Hidrojen Gaz Algılama Özelliklerinin İncelenmesi", *Journal of Polytechnic*, 19(3): 223-229, (2016).
- [9] Kumar V., Singh K., Sharma J., Kumar A., Vij A. and Thakur A., "Zn-doped SnO₂ nanostructures: structural, morphological and spectroscopic properties", *J. Mater. Sci.: Mater. Elektron*, 28(24): 18849–18856, (2017).
- [10] Saadeddin I., Hilal H.S., Pecquenard B., Marcus J., Mansouri A., Labrugere C., Subramanian M.A. and Campet G., "Simultaneous doping of Zn and Sb in SnO₂ ceramics: Enhancement of electrical conductivity", *Solid State Sci.*, 8(1): 7-13, (2006).
- [11] Guan Y., Wang D., Zhou X., Sun P., Wang H., Ma J. and Lu G., "Hydrothermal preparation and gas sensing properties of Zn-doped SnO₂ hierarchical architectures", *Sens. Actuators B*, 191: 45-52, (2014).
- [12] Gupta P., Sharma S.K., A study of oxygen gas sensing in Zn-doped SnO₂ nanostructures, *Mater. Res. Express*, 4: 065010, (2017).
- [13] Singh D., Singh Kundu V. and Maan A. S., "Structural, morphological and gas sensing study of zinc doped tin oxide nanoparticles synthesized via hydrothermal technique", *J. Mol. Struct.*, 1115: 250-257, (2016).
- [14] Galioglu S., Karaduman I., Çorlu T., Akata B., Yıldırım M. A., Ateş A. and Acar S., "Zeolite A coated Zn_{1-x}Cu_xO MOS sensors for NO gas detection", *J. Mater. Sci.: Mater. Elektron*, 29(2): 1356-1368, (2018).
- [15] Çorlu T., Karaduman I., Galioglu S., Akata B., Yıldırım M.A., Ates A. and Acar S., "Low level NO gas sensing properties of Cu doped ZnO thin films prepared by SILAR method", *Mater. Lett.*, 212: 292–295 (2018).
- [16] Soltabayev B., Karaduman Er I., Sural H., Coşkun A, Yıldırım M.A., Ateş A. and Acar S., "Influence of Ni doping on the nitric oxide gas sensing properties of Zn_{1-x}Ni_xO thin films synthesized by silar method", *Mater. Res. Express* 6: 086419, (2019).
- [17] Karaduman Er I., Çağırtekin A.O., Çorlu T., Yıldırım M.A., Ateş A. and Acar S., "Low-level NO gas sensing properties of Zn_{1-x}Sn_xO nanostructure sensors under UV light irradiation at room temperature", *Bull. Mater. Sci.*, 42(32), (2019).
- [18] Vermaa M., Dwivedib P. K. and Das B., "Structure–property correlation of pure and Sn-doped ZnO nanocrystalline materials prepared by co-precipitation", *Journal of Experimental Nanoscience*, 10(6): 438–448, (2015).
- [19] Zhang Z., Yi J.B., Ding J., Wong L.M., Seng H.L. and Wang S.J. "Cu-Doped ZnO Nanoneedles and Nanonails: Morphological Evolution and Physical Properties", *J. Phys. Chem. C*, 112: 9579, (2008).
- [20] Patil A., Dıghavkar C., and Borse R., "Al Doped ZnO Thick Films As CO₂ Gas Sensors", *J. Optoelectron Adv. M.*, 13(10): 1331-1337, (2011).
- [21] Zhou Q., Chen W., Xu L., Kumar R., Gui Y., Zhao Z., Tang C. and Zhu S., "Highly sensitive carbon monoxide (CO) gas sensors based on Ni and Zn doped SnO₂ nanomaterials", *Ceram. Int.* 44: 4392–4399, (2018).
- [22] Zheng L., Xu T., Li G. and Q Yin, "Influence of thickness on oxygen-sensing properties of TiO₂ thin films on Al₂O₃," *J. Appl. Phys., Part 1* 41: 4655-4658, (2002).
- [23] Hossein-Babari F. and Orvatinia M., "Analysis of thickness dependence of the sensitivity in thin film resistive gas sensors", *Sens. Actuators B* 89: 256-261, (2003).
- [24] Christoulakis S., Suche M., Koudoumas E., Katharakis M., Katsarakis N. and Kiriakidis G., "Thickness influence on surface morphology and ozone sensing properties of nanostructured ZnO transparent thin films grown by PLD", *Appl. Surf. Sci.*, 252: 5351-5354, (2006).
- [25] Çorlu T., Karaduman I., Yildirim M.A., Ateş A. and Acar S., "Effect of Doping Materials on the Low-Level NO Gas Sensing Properties of ZnO Thin Films", *J. Electron. Mater.*, 46(7): 3995–4002, (2017).
- [26] Najafi V., Zolghadr S. and Kimiagar S., "Remarkable reproducibility and significant sensitivity of ZnO nanoparticles covered by Chromium (III) oxide as a hydrogen sulfide gas sensor", *Optik - International Journal for Light and Electron Optics* 182: 249–256, (2019).
- [27] Chang B.-Y., Wang C.-Y., Lai H.-F., Wu R.-J. and Chavali M., "Evaluation of Pt/In₂O₃–WO₃ nano powder ultra-trace level NO gas sensor", *Journal of the Taiwan Institute of Chemical Engineers* 45: 1056–1064, (2014).
- [28] Yulianto B., Ramadhani M.F. and Wieno H. Nugraha. "Fabrications of NO Gas Sensors Based on ZnO Nanorod Thin Films", *International Journal of Materials Science and Engineering* 2(1): 1, (2014)
- [29] Wu M.-R., Li W.-Z., Tung C.-Y., Huang C.-Y., Chiang Y.-H., Liu P.-L. and Horng R.-H., "NO gas sensor based on ZnGa₂O₄ epilayer grown by metalorganic chemical vapor deposition", *Scientific Reports* 9: 7459, (2019).

- [30] Akamatsu T., Itoh T., Izu N. and Shin W., “NO and NO₂ Sensing Properties of WO₃ and Co₃O₄ Based Gas Sensors”, *Sensors* 13: 12467-12481, (2013)
- [31] Lin, C.-H., Chang, S.-J., and Hsueh, T.-J., “A WO₃ Nanoparticles NO Gas Sensor Prepared by Hot-Wire CVD”. *IEEE Electron Device Letters*, 38(2): 266–269, (2017).
- [32] Lin, C.-Y., Chen, J.-G., Feng, W.-Y., Lin, C.-W., Huang, J.-W., Tunney, J. J., and Ho, K.-C. “Using a TiO₂/ZnO double-layer film for improving the sensing performance of ZnO based NO gas sensor”. *Sens. Actuators B*, 157(2): 361–367, (2011).
- [33] Fang Y.Y., Lin C.W., Tunney J.J., and Ho K.C.. “Fabrication of NO_x gas sensors using In₂O₃– ZnO composite films”. *Sens Actuators B*, 146: 28–34. (2010).