Low concentration NO gas detection of SnO$_2$ and Zn$_{0.50}$Sn$_{0.50}$O sensors

SnO$_2$ ve Zn$_{0.50}$Sn$_{0.50}$O sensörlerinin düşük NO gaz konsantrasyonu algılama özellikleri

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SnO₂ ve Zn₀.₅₀Sn₀.₅₀O Sensörlerinin Düşük NO Gaz Konsantrasyonu Algılama Özellikleri

Araştırma Makalesi / Research Article

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ÖZ

Bu çalışmada, SnO₂ ve Zn₀.₅₀Sn₀.₅₀O örnekleri Ardıçlı İyonik Katman Adsorpsiyon ve Reaksiyon yöntemleriyle 3 farklı döngü 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. Sonuç olarak, SnO₂ sensörüne kıyasla daha yüksek algılama performansı gösterildi. 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. Diğer yandan, Zn₀.₅₀Sn₀.₅₀O sensörünün 50 ppb NO gaz konsantrasyonu için gösterdiği duyarlılık % 3.01, % 3.74 ve % 4.16 olarak elde edilmiştir. Ölçüm sonuçları, numunelerin gaz algılaması özelliklerinde katkılama ve üretim döngüsüne bağlı olarak değiştiğini gösterdi.

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

Low Concentration NO Gas Detection Of SnO₂ And Zn₀.₅₀Sn₀.₅₀O Sensors

ABSTRACT

In this study, the gas sensing properties of SnO₂ and Zn₀.₅₀Sn₀.₅₀O 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 105 °C. The sensors were proved to have acceptable responses towards 50 ppb NO gas. Zn₀.₅₀Sn₀.₅₀O sensor exhibited improved sensing performance at working temperature of 105 °C compared to SnO₂ sensor. The responses of SnO₂ sensor 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 Zn₀.₅₀Sn₀.₅₀O 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 colorless, 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 as 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 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 great challenges [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 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, SnO$_2$ 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 SnO$_2$ sensors with Zn exhibited the high responses which was about 3.2 times higher compared to the pure SnO$_2$ [11]. Gupta et al. have shown that Zn-doping has been found to increase the sensitivity of oxygen than the pure SnO$_2$ [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 SnO$_2$ [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 substrates 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 SnO$_2$ 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 SnO$_2$ and Zn$_{0.50}$Sn$_{0.50}$O samples were produced by SILAR method. Before producing the samples, the metal conacts 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 ZnCl$_2$, SnCl$_4$, and NH$_3$ are mixed, reactions occur and a complex of [Zn(NH$_3$)$_2$]$^{2+}$ and ([Sn(NH$_3$)$_4$]$^{4+}$ (pH=10) is formed. Substrate material was suspended in [Zn(NH$_3$)$_2$]$^{2+}$ and ([Sn(NH$_3$)$_4$]$^{4+}$ 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$_x$O films were grown on substrates. (‘x’ is defined as doping ratio for producing samples). Possible reactions were given as follows:

\[ \text{ZnCl}_2 + 2\text{NH}_3\text{OH} \rightarrow \text{Zn(OH)}_2 + 2\text{NH}_4^+ + \text{Cl}^- \] \hspace{1cm} (1)

\[ \text{Zn(OH)}_2 + 4\text{NH}_4^+ \rightarrow [\text{Zn(NH}_3)_2]^{2+} + 2\text{H}_2\text{O} + 2\text{H}^+ \] \hspace{1cm} (2)

\[ \text{SnCl}_4 + 2\text{NH}_3\text{OH} \rightarrow \text{Sn(OH)}_2 + 2\text{NH}_4^+ + \text{Cl}^- \] \hspace{1cm} (3)

\[ \text{Sn(OH)}_2 + 4\text{NH}_4^+ \rightarrow [\text{Sn(NH}_3)_4]^{4+} + 2\text{H}_2\text{O} + 2\text{H}^+ \] \hspace{1cm} (4)
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 SnO_{2} 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 Kα λ=1.5405Å 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.

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 SnO_{2}. 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 SnO_{2} reveals that all the peaks are in good agreement with the JCPDS data belonging to tetragonal phase. (JPCDS Card No:41-1445) [17].
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 responses of SnO$_2$ and Zn$_{0.50}$Sn$_{0.50}$O samples 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 $105^\circ$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 3. The SEM images of SnO$_2$ 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)

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 $105^\circ$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 SnO$_2$ (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 surly affects the sustainability and reliability of the sensor [25]. Hence, Fig 7. depicts the reproducibility of Zn$_{0.30}$Sn$_{0.70}$O (a) and SnO$_2$ (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.

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, largeing 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]:

$$\text{NO}_{(gaz)} + e^- \rightarrow \text{NO}_{(ads)}^-$$  \hspace{1cm} (5)

$$\text{NO}_{(ads)}^- + \text{O}_2 \rightarrow \text{NO}_3^{-}_{(ads)}$$ \hspace{1cm} (6)

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

<table>
<thead>
<tr>
<th>Materials</th>
<th>Producing Method</th>
<th>Gas Concentration</th>
<th>Sensing Response</th>
<th>Operating Temperature</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO nanowire thin films</td>
<td>Dip coating</td>
<td>70 ppm</td>
<td>90</td>
<td>200°C</td>
<td>[28]</td>
</tr>
<tr>
<td>ZnO:SnO nanocomposite thin films</td>
<td>Metalorganic chemical vapor deposition</td>
<td>6.25 ppm</td>
<td>22.21</td>
<td>500°C</td>
<td>[29]</td>
</tr>
<tr>
<td>CuO powder</td>
<td>Mixed with an organic dispersant for obtaining a paste</td>
<td>1 ppm</td>
<td>1.2</td>
<td>200°C</td>
<td>[30]</td>
</tr>
<tr>
<td>WO3 nanoparticles</td>
<td>Electroformed assisted hot wire system</td>
<td>350 ppm</td>
<td>15.93</td>
<td>150°C</td>
<td>[31]</td>
</tr>
<tr>
<td>ZnO:SnO nanocomposite thin films</td>
<td>Screen-printing</td>
<td>10 ppm</td>
<td>50/150</td>
<td>320°C</td>
<td>[32]</td>
</tr>
<tr>
<td>SnO:ZnO</td>
<td>The chemical bath precipitation</td>
<td>10 ppm</td>
<td>8</td>
<td>100°C</td>
<td>[33]</td>
</tr>
<tr>
<td>ZnSn3O5</td>
<td>SILAR</td>
<td>50 ppm</td>
<td>3.37</td>
<td>105°C</td>
<td>In this work</td>
</tr>
</tbody>
</table>

With the doping of Zn, Zn atoms in substitutional Sn positions (ZnSn0.50Sn0.50) favor the formation of VO due to charge compensation [21]. It is probably because Zn atom 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, ZnSnO5 exhibited the higher responses compared to the pure SnO2.

### 4. CONCLUSION

In this work, SnO2 and Zn0.50Sn0.50O sensors have been grown by SILAR method. The working temperature was found at 105°C. After this temperature, the responses began to decrease. The response of SnO2 and Zn0.50Sn0.50O to NO gas as a function of gas concentration, 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 Zn0.50Sn0.50O 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.

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