Annealing Effects on Gas Sensing Response of Ga-Doped ZnO Thin Films

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ABSTRACT: The high thermal conductivity, high electron mobility, the direct wide band gap, and large exciton binding energy of zinc oxide (ZnO) make it appropriate for a wide range of device applications like light-emitting diodes, photodetectors, laser diodes, transparent thin-film transistors, and so forth. Among the semiconductor metal oxides, zinc oxide (ZnO) is one of the most commonly used gas-sensing materials. The gas sensor made of nanocomposite ZnO and Ga-doped ZnO (ZnO:Ga) thin films was developed by the sol–gel spin coating method. The gas sensitivity of gallium-doped ZnO thin films annealed at 400, 700, and 900 °C was studied for ethanol and acetone gases. The variation of electrical resistance of gallium-doped ZnO thin films with exposure of ethanol and acetone vapors at different concentrations was estimated. Ga:ZnO thin films annealed at 700 °C show the highest sensitivity and shortest response and recovery time for both ethanol and acetone gases. This study reveals that the 5 at. % Ga-doped ZnO thin film annealed at 700 °C has the best sensing property in comparison to the film annealed at 400 and 900 °C. The sensing response of ZnO:Ga thin films was found higher for ethanol gas in comparison to acetone gas.

1. INTRODUCTION

It is well known that the electrical properties of semiconductors are sensitive to the surrounding gases. Initially, it was not taken seriously as the results were not sufficiently reproducible.1,2 Taguchi developed the first commercial device using the sensitivity of SnO2 to absorb the gases.3 The use of compressed powder of SnO2 rather than a single crystal substantially improved the sensitivity, and a practical device was developed for detection of gases in the air. The semiconductor sensor is based on the change in semiconductor conductance due to reaction between the semiconductor and the gases in the atmosphere. The gas sensing mechanisms are based on the assumption that the electronic density is removed due to adsorption of oxygen on the surface of the oxide, thus decreasing the conductivity of the material. The gas molecules come into contact with the semiconductor surface, interact with oxygen, and lead to inverse charge transference.3

Zinc oxide (ZnO) is considered as a promising material for gas sensors.5,6 This is one of the earliest discovered materials for gas sensing, and there are various reports concerning the sensing properties of ZnO, realized using its powdered samples.7,8 Recently, studies over ZnO nanorods and ZnO thin films had been performed for their sensing efficiencies.9–16 The work on the development of the selective gas sensor using pure and doped n-type zinc oxide thin films is in progress.17–19 Although the pure ZnO films show n-type electrical conductivity, their properties are altered by adsorption of O2, CO2, and water in a humid environment. The pure form of ZnO is generally too resistive for transport conducting oxide applications and requires donor dopants. The doping elements produce the defects in ZnO thin films and thus enhance the sensing properties. Gallium doping results in shallow donor states below the ZnO conduction band minima that are ionized at room temperature to increase carrier concentration and therefore reduce electrical resistivity.20,21

Due to increased levels of toxic and harmful gases in the environment, we need a suitable material to develop fast response sensors for their monitoring. In search of such materials, the nanostructured ZnO thin films have drawn considerable attention of researchers.10–14,17 The objective of the present investigation is to develop the highly sensitive gas sensor for ethanol and acetone gases. For this purpose, the response and recovery time, sensitivity, and selectivity of Ga-doped ZnO thin films modified by thermal annealing are analyzed. The gas sensing mechanism of the SMO sensors has two main functions, one being the receptor and the other the...
transducer. The receptor involves the recognition of a target gas at the gas–solid interface, which includes electronic changes to the surface of metallic oxides. The transducer function involves the transduction of the surface phenomenon into a change of electric resistance in the sensor. The dopant plays an important role in the receptor function by altering the catalytic reactivity and morphology of deposited films. It also plays a role in the transducer function by affecting the various factors like change in the microstructure and morphology, formation of stoichiometric solid solutions, change in activation energy, generating oxygen vacancy, and changing the electronic structure.22 However, the role of dopants in gas sensing is poorly understood, i.e., how intrinsic properties of dopants (atomic and ionic radii/charge state) affect the electronic structure, defects, and surface area, and thus the sensing mechanism. Among the various dopants, gallium (Ga) is found to be a successful and promising dopant due to some mechanism. Among the various dopants, gallium (Ga) is found to be a successful and promising dopant due to some advantages, such as rather similar ionic and covalent radii (0.62 and 1.26 Å, respectively) compared to those of Zn (0.74 and 1.34 Å, respectively). Hence, Ga3+ ions can substitute Zn2+ without any lattice distortion and cause free stress in the ZnO material.23 In addition to this, n-type behavior (donor doping) appears with gallium as a ZnO dopant. Ga doping can produce a large number of donor electrons, which improves the conductivity of ZnO. It induces defects and reduces the size of the ZnO grain, which influences the sensitivity, response time, and stability of the gas sensor.24 The detail significance and findings of this study are discussed in this paper.

2. MATERIALS AND METHODS

2.1. Sample Preparation. Gallium-doped ZnO thin films were produced by the sol–gel spin coating method over quartz substrates. Zinc acetate dehydrate Zn(CH3COO)2⋅H2O was used as a starting material. 2-Methoxyethanol and monoethanolamine (MEA) were used as a solvent and stabilizer, respectively. The ZnO precursor solution was prepared by dissolving zinc acetate dehydrate in 2-methoxyethanol. The total concentration of the sol was maintained at 0.5 mol/L. MEA was dissolved into the solution. The molar ratio of diethanolamine/Zn was fixed at 1:0. For the preparation of 5 at % Ga-doped ZnO thin films, gallium nitrate was dissolved in the solution. The mixture solution was stirred at 60 °C for 2 h. A transparent and homogeneous solution was obtained after 72 h. This solution was then spin-coated over the quartz substrates at 2800 rpm. After deposition, the films were dried in air at 220 °C for 10 min over a hot plate, and the process was repeated for the desired thickness. These films were modified by thermal annealing at various temperatures. For thermal-annealed modification, the synthesized films of ZnO:Ga thin films were annealed at 400, 700, and 900 °C in an oxygen environment for 1 h in a microprocessor-controlled furnace. The measurement of gas sensing response was carried out in a test chamber consisting of a sample holder, a small temperature-controlled oven, a circulating fan, and a simple potentiometer arrangement.15 The gas-induced resistance variation in the Ga-doped ZnO semiconductor can be calculated when exposed with the target gas ethanol and acetone at different concentrations.

2.3. Resistance Measurement. A conventional potentiometer arrangement has been used for the resistance measurement. In this technique, a potential difference of 12 V is applied between the gold-painted electrodes of Ga-doped ZnO thin films. In the series of thin-film resistances, a load resistance of 1000 kΩ was conceded and when the target gas interacts with the thin-film surface, the resistance of the film changes. All the variations in the voltage signal across the resistance Rg connected in series with the sensor were recorded with Keithley Data Acquisition Module KUSB-3100 on a computer. The sensor response magnitude was determined as the Rgas/Rair ratio, where Rgas and Rair are the resistances of the sensor in the air—gas mixture and ambience air, respectively.

3. RESULTS AND DISCUSSION

In the present investigation, the gas sensing property of thermally annealed ZnO-Ga thin films has been studied. The ZnO:Ga thin films were annealed at 400, 700, and 900 °C. These modified ZnO:Ga thin films were exposed at the different concentration of ethanol and acetone gas vapors for gas sensing applications.

3.1. Sample Thickness and Structural Characterization. The thickness of 5 at. % Ga-doped ZnO films annealed at 700 °C were examined with Rutherford backscattering spectrometry (RBS) analysis. Experimental spectra are best fitted with the Rutherford Universal Manipulation Program (RUMP) to measure the thickness of the films as shown in Figure 1.

![Figure 1. RBS experimental and simulated plot of 5 at. % Ga-doped ZnO (annealed at 700) thin films for determining the film thickness.](https://doi.org/10.1021/acs.omega.1c00984)

The simulation suggests that the thickness of the film is around 745 ± 15 nm. Figure 2 shows the grazing incidence X-ray diffraction (XRD) pattern of the samples (5 at. % ZnO:Ga).

The diffraction intensities corresponding to the (101), (002), (100), (102), and (110) planes match with the ZnO hexagonal wurtzite structure. It is confirmed that the pure crystalline ZnO phase is present in the sample and no signs of amorphization and other structural phases are present.
However, we observed the variation in peak intensities and full width at half-maximum for the samples annealed at various temperatures. It could be observed that peak intensities increase with increasing temperature due to improvements of the stoichiometry and crystallite quality of the samples. For further studies, the average crystallite size was estimated from the dominating diffraction peak (101) using Scherer’s formula.\textsuperscript{23} The lattice parameters “a” and “c” of the films are calculated from the diffraction peaks (002) and (101) by using the relation for hexagonal structure of ZnO.\textsuperscript{23} All the measured parameters are tabulated in Table 1. It is evident from the values reported in Table 1 that the ethanol gas sensing response of ZnO:Ga (700 °C annealed) slightly increases from 0.35 to 0.50 for the temperature between 100 and 200 °C.

The gas sensing response is restricted within this temperature range because the gas molecules do not possess sufficient thermal energy to react with the adsorbed oxygen species on the surface, and hence, the speed of the chemical reaction is slow.

### 3.2. Gas Sensing Characteristics of 5 at. % ZnO:Ga Annealed at 700 °C

The ZnO:Ga thin film was annealed at 700 °C for the gas sensing properties. The ZnO:Ga-based metal oxide semiconductor was exposed with acetone and ethanol gas vapors at different concentrations. The 5 at. % ZnO:Ga thin film was first optimized at different operating temperatures for ethanol gas of 250 ppm. Figure 3 shows the response of the 5 at. % Ga-doped ZnO thin film (700 °C annealed) for a 250 ppm ethanol concentration at different operating temperatures.

The gas sensing response of the ZnO:Ga thin-film sensor was found to be maximum at the operating temperature of 450 °C. Hence, this Ga-doped ZnO thin-film sensor is optimized at 450 °C. It is observed that optimizing temperature depends on the type of gases, the mechanism of dissociation, and further chemisorption of the gas on the surface of a particular sensor. The formation of charged oxygen ions on the surface of oxide is another factor responsible for the temperature-dependent sensitivity of the sensor. The ZnO thin film with the additive gallium shows fast response to ethanol and acetone, which shows the importance of additives in detection of a specific gas. The presence of gallium enhances the sensitivity and response rate of the sensor due to the electronic interaction between the sensitizer and the material. Figure 4 shows the variation of electrical resistance of the ZnO:Ga thin film as a function of the temperature.

![Figure 3. Response of the 5 at. % Ga-doped ZnO thin film (700 °C annealed) for a 250 ppm ethanol concentration at different operating temperatures.](image)

It is observed that the electrical resistance of the thin film first increases from $2.0 \times 10^9$ to $2.5 \times 10^9$ Ω with the temperature from 300 to 350 °C (region I). This change is attributed to the adsorption of atmospheric oxygen on the surface of the ZnO:Ga thin film. In region II, in the temperature range of 350–500 °C, the electrical resistance of the thin film decreases from $2.0 \times 10^9$ to $1.5 \times 10^8$ Ω. This change is attributed to the thermal excitation of electrons into the conduction band.

![Figure 4. Variation of electrical resistance of the 5 at. % Ga-doped ZnO thin film annealed at a temperature of 700 °C.](image)

| s. no. | operating temperature (°C) | ethanol (250 ppm) (700 °C) | acetone (250 ppm) (400 °C) |
|-------|---------------------------|-----------------------------|-----------------------------|
| 1     | 100                       | 0.35                        | NA                          |
| 2     | 150                       | 0.40                        | NA                          |
| 3     | 200                       | 0.50                        | NA                          |
| 4     | 250                       | 1.44                        | NA                          |
| 5     | 300                       | 3.52                        | NA                          |
| 6     | 350                       | 5.12                        | 1.20                        |
| 7     | 400                       | 6.99                        | 1.30                        |
| 8     | 450                       | 21.00                       | NA                          |
| 9     | 500                       | 4.75                        | NA                          |
Figure 5 shows the response characteristic of the sensor film as a function of ethanol concentration at an operating temperature of 450 °C. It is observed that the sensing response of the thin film increases linearly from 8.00 to 22.22 with increasing gas concentration from 50 to 250 ppm, respectively; however, it increases rapidly to 41.0 for the higher gas concentration. Further, the response and recovery characteristics of the sensor at the operating temperature are shown in Figure 6. The sensor shows a fast response time of ~11 s for ethanol at a 250 ppm concentration but a longer recovery time of ~30 s.

The acetone and ethanol gas sensing responses of the Ga-doped ZnO thin film annealed at 400, 700, and 900 °C are shown in Table 2. The sensing response of the thin film linearly increases from 8.00 to 22.22 with the increase of the gas concentration from 50 to 250 ppm, respectively, but the sensing response increases gradually from 22.22 to 27 for gas concentrations between 250 and 500 ppm, respectively (Table 2). Again, with the increase of the ethanol gas concentration from 500 to 750 ppm, the sensing response increases very rapidly to 41.0, but further by impressing the gas concentration up to 1000 ppm, the sensing response decreases to 38.0. Figure 6 also shows the response characteristic of the film (700 °C annealed) as a function of acetone concentration at an operating temperature of 450 °C. It is clear that the gas sensing response of acetone gas for the Ga-doped ZnO thin film (annealed at 700 °C) initially increases from 10.0 to 16.0 between 50 and 100 ppm gas concentrations, but the sensing response decreases to 9.00 at a 250 ppm concentration. From a gas concentration of 250 ppm to 750 ppm, the sensing response increases sharply from 9.0 to 46.0 after a 750 ppm gas concentration.

Figures 7 and 8 show the response and recovery characteristics of the Ga-doped ZnO (700 °C annealed) thin film at an operating temperature of 450 °C for a 250 ppm concentration of ethanol and acetone gas. The sensor shows fast response for acetone and ethanol at a 250 ppm concentration but a longer recovery time. For ethanol gas, the developed thin film has a response time and a recovery time of ~11 and ~30 s, respectively, while for acetone gas exposure, it has a response time and a recovery time of ~7 and ~20 s, respectively. These

Table 2. Gas Sensing Response of ZnO:Ga (Annealed at 400, 700, and 900 °C) with Exposure of Ethanol and Acetone Gas

| s. no. | gas concentration (ppm) | acetone (400 °C) | acetone (700 °C) | ethanol (700 °C) | acetone (900 °C) | ethanol (900 °C) |
|--------|-------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1      | 50                      | NA              | 10.00           | 8.00            | 3.29            | 4.01            |
| 2      | 100                     | 1.25            | 16.00           | 12.00           | 4.49            | 5.00            |
| 3      | 250                     | 1.26            | 9.00            | 22.22           | 3.50            | 6.00            |
| 4      | 500                     | 1.57            | 26.00           | 27.00           | 7.00            | 7.00            |
| 5      | 750                     | 2.07            | 41.00           | 41.00           | 8.48            | 10.00           |
| 6      | 1000                    | NA              | 46.00           | 38.00           | 9.00            | 10.00           |
results show that the developed thin film is a better sensor for acetone gas in comparison to ethanol gas. This thin film also has higher sensing response for acetone in comparison to ethanol. The sensitivity of the ZnO:Ga thin film increases sharply with the acetone gas concentration.

Figures 9 and 10 show the variation of electrical resistance of Ga-doped thin films with the exposure of acetone and ethanol gases. It is evident from Figure 9 that the electrical resistance of the thin film decreases from $5 \times 10^9$ to $2.5 \times 10^8 \, \Omega$ with the exposure of acetone gas, while it decreases from $1.5 \times 10^9$ to $2.5 \times 10^8 \, \Omega$ for the ethanol gas exposure. When the ZnO:Ga thin film is exposed at different concentrations of ethanol, the film resistance decreases and increases again with recovery in the air. The gas sensing response increases with the increase of the gas concentration because of the coverage of the molecules on the larger surface of the film resulting in the sufficient availability to adsorb oxygen species on the sensing sites.

It is well known that oxygen chemisorbs on the surface in a molecular ($O_2^{-}$) and atomic form ($O^{-}$) within the temperature ranging between 100 and 500 °C. $O_2^{-}$ dominates at temperatures below 200 °C because of its lower activation energy, while $O^{-}$ dominates at higher temperatures.

\[ O_2(\text{air}) \rightleftharpoons O_2(\text{ads}) \rightleftharpoons O_2^{-}(\text{ads}) + e^- \rightleftharpoons O_2^{-}(\text{ads}) + e^- \]
\[ \rightleftharpoons 2O^{-}(\text{ads}) \]

The sensing is a complex phenomenon and occurs on the surface of the semiconductor. Rothschild and Komen have simulated the sensing response with various sensing parameters. However, the surface reactivity of particles was found to increase rapidly with the increase in the surface-to-bulk ratio. Figure 11 shows the temperature dependence of conductance of the Ga-doped ZnO thin film (annealed at 700 °C).

\[ C = C_0 e^{-qV_s/kT} \]

where $C_0$ is a factor, which includes the bulk inter-granular conductance constant, $T$ is the absolute temperature, $k$ is Boltzmann’s constant, and $qV_s$ is the potential energy barrier at the interface of two neighboring grains.

It was observed that the height of the energy barrier between neighboring grains in a material controls conduction and sensitivity of the material. The activation energy of the semiconductor plays an important role in the gas sensing mechanism and can be calculated using the following relation.
generates defect levels within the band gap, reduces the reaction activation energy, and thus changes the resistance. The low activation energy contributed to improve the gas sensing characteristics.

3.3. Gas Sensing Characteristics of 5 at. % ZnO:Ga Annealed at 900 °C. The 5 at. % doped ZnO:Ga thin film annealed at 900 °C was also exposed by ethanol and acetone gases to study the gas sensing response. This sensor is also optimized at 450 °C. It shows that with annealing of Ga-doped ZnO, the optimization temperature remains invariant. Figure 12 shows the response characteristic of the thin film (900 °C annealed) as a function of ethanol and acetone concentrations at an operating temperature of 450 °C.

![Figure 12](https://example.com/figure12.png)

Figure 12. Response characteristic of the film (900 °C annealed) as a function of ethanol and acetone concentrations at an operating temperature of 450 °C.

It is evident that the sensing response of the ZnO:Ga thin film (900 °C annealed) to ethanol gas first increases gradually from 4.01 to 7.0 between 50 and 500 ppm gas concentrations, which further increases sharply to 10.0 at a 750 ppm gas concentration, and thereafter, the response becomes constant (Table 2). A similar trend was observed for acetone gas.

The sensing response of the thin film for acetone gas slowly increases from 3.29 to 4.49 between 50 and 100 ppm gas concentrations and then decreases to 3.50 at a 250 ppm gas concentration (Table 2). Further by increasing the gas concentration from 250 to 500 ppm, the sensing response increases sharply to 7.0, which becomes 9.0 at a 1000 ppm gas concentration. Figures 13 and 14 show the response—recovery characteristics of the Ga-doped ZnO (900 °C annealed) thin film at the operating temperature of 450 °C.

![Figure 13](https://example.com/figure13.png)

Figure 13. Response—recovery characteristics of the Ga-doped ZnO (900 °C annealed) thin film at the operating temperature of 450 °C for ethanol gas.

![Figure 14](https://example.com/figure14.png)

Figure 14. Response—recovery characteristics of the Ga-doped ZnO (900 °C annealed) thin film at the operating temperature of 450 °C for acetone gas.

The response and recovery times of the sensor are defined as the time period of the gas exposure and the gas removal, respectively. The response and recovery times of the 5 at. % gallium-doped ZnO thin film with the exposure of ethanol gas are ~20 and ~34 s, respectively, while those for acetone gas are ~10 and ~20 s, respectively. These results show that the developed thin films have short response and recovery times for acetone gas.

Figure 15 shows the variation of electrical resistance of the Ga-doped ZnO thin film, annealed at 900 °C, with time for different concentrations of ethanol and acetone gases.

![Figure 15](https://example.com/figure15.png)

Figure 15. Variation of electrical resistance of the ZnO:Ga-doped thin film (annealed at 900 °C) with time for different concentrations of ethanol and acetone gases.

The electrical resistance of this film decreases from $1.2 \times 10^7$ to $2 \times 10^6$ and $1.3 \times 10^7$ to $4 \times 10^6$ Ω with exposure of ethanol and acetone gas, respectively. The ability of a sensor to...
measure a single component in the presence of other components is known as the selectivity of the sensor. The selectivity of a sensor is assessed by following relation

\[
\text{selectivity} = \frac{\text{sensitivty of gas 1}}{\text{sensitivty of gas 2}}
\]

The selectivity of the sensor is the ratio of sensitivities between the gases to be detected over the gases not to be detected in equivalent concentrations. The results obtained from the present investigations show that the sensor developed from the Ga-doped ZnO thin film has higher selectivity for acetone gas in comparison to ethanol gas.

3.4. Gas Sensing Characteristics of 5 at. % ZnO:Ga Annealed at 400 °C. The 5 at. % gallium-doped ZnO thin film annealed at 400 °C was also exposed with ethanol and acetone gas vapors for gas sensing characteristics. Figure 16 shows the sensing response of the 5 at. % Ga-doped ZnO thin film (400 °C annealed) to a 250 ppm acetone gas concentration at different operating temperatures. The observed values of the sensing response of the Ga-doped ZnO thin film (400 °C annealed) at different operating temperatures for acetone are shown in Table 1. The film does not show any response below the temperature of 350 °C. At the operating temperature of 350 °C, the thin film shows a small response of 1.2, and the maximum response of 1.30 was observed at an operating temperature of 400 °C. Thus, the 5 at. % gallium-doped ZnO thin film annealed at 400 °C is optimized at 400 °C.

Figure 17 shows the response of the 5 at. % Ga-doped ZnO thin film (400 °C annealed) for different concentrations of acetone. The observed values of the sensing response of the Ga-doped ZnO thin film (annealed at 400 °C) for ethanol and acetone are shown in Table 2. From the figure, it is clear that the sensing response of the Ga-doped ZnO thin film linearly increases with increasing gas concentration.

Figures 18 and 19 show the response-recovery characteristics of the Ga-doped ZnO (400 °C annealed) thin film at the operating temperature of 400 °C for ethanol and acetone gases at a 250 ppm concentration. For the ethanol gas vapors, the thin film has a response time and a recovery time of ~30 and ~40 s, respectively, while for ethanol vapor, they are ~28 and ~32 s, respectively. For acetone, the sensor has short response and recovery times.

Figure 20 shows the variation of electrical resistance of the ZnO:Ga-doped thin film (annealed at 400 °C) with time for a 250 ppm concentration of ethanol and acetone gases.
These equations reveal that acetone could release more electrons ($8e^{-}$) than ethanol ($6e^{-}$) when the same concentration of the gas reacted with oxygen ions of the sensor, and thus, a higher response to acetone was observed. Further, the response of the sensor could be related to the surface area. The surface area could be calculated theoretically using the relation \( SA = \frac{6}{(d^* \rho)} \), where \( d \) is the particle size and \( \rho \) is the density of ZnO (5.606 g/m$^3$).\(^{22}\) The values of the surface area for different \( d \) values (XRD crystallite size) are 116.3, 97, 62, and 31.4 m$^2$/g. Table 2 shows that maximum response for both gases is obtained for 700 °C annealed samples having a surface area of 62 m$^2$/g. However, 500 and 900 °C annealed samples with surface areas of 116.3 and 31.4 m$^2$/g, respectively, have low response to the target gases. The sample annealed at 400 °C has the largest surface area but low response, which could be attributed to the larger density of the grain boundary in this sample. This may act as trapping sites for oxygen species and forms potential barriers, leading to a decrease in the carrier concentrations, which increases the resistance and hence affects the response of the sensor. For an annealing temperature of 900 °C, the sample has good crystallinity and hence less grain boundaries. However, the response is less, which could be due to less surface area available for the reaction of the target gases, hence reducing the carrier concentration. All the samples are doped with gallium (Ga) at 5 at. %, but the highest response was obtained for an annealing temperature of 700 °C. The above discussion suggests that the crystallinity of the film, the grain boundary, and surface area play an important role in the sensing mechanism.

4. CONCLUSIONS

Ga-doped ZnO films prepared by sol–gel spin coating annealed at 400, 700, and 900 °C are investigated for sensing of two target gases, ethanol and acetone. Among these annealed films, the Ga-doped ZnO thin film annealed at 700 °C shows the highest sensitivity and the shortest response and recovery times for both ethanol and acetone gases in comparison to the films annealed at 400 and 900 °C. This film has the response and recovery times of ~11 s and ~30 s for ethanol gas and ~7 s and ~20 s for acetone, respectively. The response and recovery of the sensor were better for acetone. It is also observed that film stoichiometry, crystallinity, grain boundary density, and surface area play an important role in the sensing mechanism. Further studies can be done for these various parameters separately to have a better understanding of the sensing mechanism.

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REFERENCES

(1) Brattain, W. H.; Bardeen, J. Surface Properties of Germanium. Bell Syst. Tech. J. 1953, 32, 1−41.
(2) Morrison, S. R. Surface Barrier Effects in Adsorption, Illustrated by Zinc Oxide. Adv. Catal. 1955, 7, 259−301.
(3) Taguchi, N. Gas Detecting Device. U.S. Patent 3,695,848 A, 1971.
(4) Islam, M. R.; Kumazawa, N.; Takeuchi, M. Chemical sensor based on titanium dioxide thick film: Enhancement of selectivity by surface coating. Appl. Surf. Sci. 1999, 142, 262−266.
(5) Hofmann, T.; Schieberle, P.; Krummel, C.; Freiling, A.; Bock, J.; Heinert, L.; Kohl, D. High Resolution Gas Chromatography/Selective Odorant Measurement by Multisensor Array (HRGC/SOMSA): a Useful Approach to Standardise Multisensor Arrays for use in the Detection of Key Food Odorants. Sens. Actuators, B 1997, 41, 81−87.
(6) Hong, H.-K.; Kwon, C. H.; Kim, S.-R.; Yun, D. H.; Lee, K.; Sung, Y. K. Portable Electronic Nose System with Gas Sensor Array and Artificial Neural Network. Sens. Actuators, B 2000, 66, 49−52.
(7) Choi, J. D.; Choi, G. M. Electrical and CO Gas Sensing Properties of Layered ZnO-CuO Sensor. Sens. Actuators, B 2000, 69, 120−126.
(8) Xu, J.; Pan, Q.; Shun, Y. a.; Tian, Z. Grain Size Control and Gas Sensing Properties of ZnO Gas Sensor. Sens. Actuators, B 2000, 66, 277−279.
(9) Kohli, N.; Singh, O.; Singh, R. C. Influence of Ph on Particle Size and Sensing Response of Chemically Synthesized Chromium Oxide Nanoparticles to Alcohols. Sens. Actuators, B 2011, 158, 259−264.
(10) Prajapati, C. S.; Sahay, P. P. Alcohol-sensing Characteristics of Spray Deposited ZnO Nano-particle Thin Films. Sens. Actuators, B 2011, 160, 1043−1049.
(11) Shishiyano, S. T.; Shishiyano, T. S.; Lupan, O. I. Sensing Characteristics of Tin-doped ZnO Thin Films as NO2 Gas Sensor. Sens. Actuators, B 2005, 107, 379−386.
(12) Suchea, M.; Christoulakis, S.; Moschovis, K.; Katsarakis, N.; Kiriakidis, G. ZnO Transparent Thin Films for Gas Sensor Applications. Thin Solid Films 2006, 515, 551−554.
(13) Sahay, P. P. Zinc Oxide Thin Film Gas Sensor for Detection of Acetone. J. Mater. Sci. 2005, 40, 4383−4385.
(14) Sahay, P. P.; Tewari, S.; Jha, S.; Shamsuddin, M. Sprayed ZnO Thin Films for Ethanol sensors. J. Mater. Sci. 2005, 40, 4791−4793.
(15) Singh, R. C.; Singh, M. P.; Singh, O.; Chandi, P. S. Influence of Synthesis and Calcination Temperature on Particle Size and Ethanol Sensing Behavior of Chemically Synthesized SnO2 Nanostructure. Sens. Actuators, B 2009, 143, 226−232.
(16) Singh, R. G.; Singh, F.; Kumar, V.; Mehra, R. M. Growth Kinetics of ZnO Nanocrystallites: Structural, Optical and Photoluminescence properties tuned by Thermal Annealing. Curr. Appl. Sci. 2011, 11, 624−630.
(17) Xianggeng, C.; Xingqin, L.; Guanyao, M. Preparation and Gas Sensitivity Properties of ZnFe2O4 Semiconductors. Sens. Actuators, B 1999, 55, 19−22.
(18) Ong, C. H.; Wang, J. H.; Gong, H.; Chan, H. S. O. Crystal Structure and Gas sensing Properties of Cu-doped Zinc Oxide. Int. J. Mod. Phys. B 2002, 16, 314−321.
(19) Stamboleva, I.; Konstantinov, K.; Vassilev, S.; Peshev, P.; Tsacheva, T. Lanthanum-doped SnO2 and ZnO Thin Films Sensitive to Ethanol and Humidity. Mater. Chem. Phys. 2000, 63, 104−108.
(20) Tamayoa-Ariola, J.; Montes Bajo, M.; Le Biavan, N.; Lefebvre, D.; Kurtz, A.; Ulloa, J. M.; Hugues, M.; Chauveau, J. M.; Hierro, A. Ga-doping of nonpolar m-plane ZnMgO with high Mg contents. J. Alloys Compd. 2018, 766, 436−441.
(21) Ponja, S. D.; Sathasivam, S.; Parkin, I. P.; Carmalt, C. J. Highly conductive and transparent gallium doped zinc oxide thin films via chemical vapor deposition. Sci. Rep. 2020, 10, 638.
(22) Wang, C.-N.; Li, Y.-L.; Gong, F.-L.; Zhang, Y.-H.; Fang, S.-M.; Zhang, H.-L. Advances in doped ZnO nanostructures for gas sensor. Chem. Rec. 2020, 20, 1553−1567.
(23) Hjiri, M.; Dahri, R.; El Mir, L.; Bonavita, A.; Donato, N.; Leonardi, S.G.; Neri, G. CO sensing properties of Ga-doped ZnO prepared by sol-gel route. J. Alloys Compd. 2015, 634, 187−192.
(24) Dey, A. Semiconductor metal oxide gas sensors: A review. Mater. Sci. Eng., B 2018, 229, 206−217.
(25) Rothschild, A.; Komem, Y. The Effect of Grain Size on the Sensitivity of Nanocrystalline Metal Oxide Gas Sensors. J. Appl. Phys. 2004, 95, 6374−6380.
(26) Madou, M. J.; Morrison, S. R. Chemical Sensing with Solid State Services; Academic press: London, 1989.
(27) Wang, J.; Yang, J.; Han, N.; Zhou, X.; Gong, S.; Yang, J.; Hu, P.; Chen, Y. Highly sensitive and selective ethanol and acetone gas sensors based on modified ZnO nanomaterials. Mater. Des. 2017, 121, 69−76.