Fabrication of High Sensitive ZnO Gas Sensor for LPG Gas Detection

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Fabrication of High Sensitive ZnO Gas Sensor for LPG Gas Detection

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Abstract

The fabricated In-doped ZnO gas sensors with different ratios (1, 5 and 10 %) were successfully synthesized via sol gel technique. ZnO is a sensitive material to different kinds of gases especially to Liquefied Petroleum Gas (LPG). The morphological structures of the prepared ZnO were revealed using a scanning electron microscope (SEM). X-ray diffraction (XRD) patterns exhibited a highly crystallized wurtzite structure and were used for identifying phase structure and chemical state of both ZnO and ZnO doped with In. The gas sensitivity and voltage are measured as a function of temperature for the fabricated In-doped and un-doped ZnO gas sensor devices for the LPG gas. The maximum sensitivity is recorded at Zn/In = 95:5 is 111%. This concentration has a good voltage variation. By increasing the load resistances the voltage will decreases.

Keywords: Arduino application, Dopant element, Gas sensor devices, Sol-gel, ZnO nanorods.

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Introduction

The semiconductor sensor type belongs to the class of solid state gas sensors. In the presence of a determinate gas the conductivity of the sensing material is changing. The working temperature for these devices which are more efficient can vary depending on properties of the sensor material selected in every case and the gas atmosphere [1].

Metal oxide semiconductor (MOS) gas sensors detect a wide variety of gases. The main advantage of the (MOS) is its life time. Theoretically, (MOS) life time is about 10 years or more in clean applications. It consists of mainly three components; sensing material (MOS), electrodes, and a heater. The common used sensing materials contain SnO$_2$, WO$_3$, In$_2$O$_3$ or ZnO [2].

Some good characteristics in ZnO gas sensor should exist such as sensitivity to different gases, ability to doping, non-toxicity, low cost and high chemical stability. ZnO is still attractive due to its easy fabrication in thin film form with various methods and its improved sensor performance by addition of dopants [3].

In this paper a study of sensitivity of fabricated the ZnO gas sensor is presented for LPG (Liquefied petroleum Gas) at nominal and high temperatures.

The development of gas sensors working to monitor combustible gases is a very important issue due to the concern for care requirements for industries and in homes, particularly for detection of LPG, which is one of widely used but potentially hazardous gases, because explosion accidents may be caused when it leaks out accidentally or by mistake. In summary the detection of LPG is essential for domestic appliances [4].

In this work doped and undoped ZnO gas sensor devices are used. These are fabricated using the sol-gel method utilized through the production of ultrafine porous powder followed by a homogenous mixing for the starting material on the molecular level.

Materials and Methods

Preparation of Doped and Undoped ZnO using Sol Gel Technique

0.1M of zinc chloride ZnCl$_2$ is prepared by dissolving 3.4 g of zinc chloride in 250 ml distilled water. A magnetic stirrer is incorporated for this purpose for about 10-15 minutes. Increase the pH for the solution to be 9 by adding NH$_3$OH to the solution. In order to prepare 1, 5 and 10 wt% In-doped ZnO; an equivalent amount of Indium chloride is added to the mixture. Then the mixture is stirred at 80°C in a glass beaker for 24 hours. The final obtained white powders are filtered and washed several times with ethanol and ultra-pure water to remove the residual salts. Then the powders centrifuged at 6000 rpm for 30 minutes, and dried at 60 °C under air atmosphere.
Preparation and Characterization of ZnO Gas Sensor

The ZnO gas sensor device is obtained as the following: mixing the synthetic ZnO nanopowder even un-doped or doped with ethanol then stirring the resulting suspension overnight to obtain colloidal suspension from ZnO. The platinum heater is obtained by depositing platinum electrodes onto the cleaned glass substrate using a sputtering machine (Turbo Sputtering RF & DC Power Supplies Deposition System Model Hummer 8.1) \((P = 100\ \text{Watt RF, } t = 5\ \text{minute})\) which use in temperature variation. ZnO suspension is applied by a wafer spinner machine \((100\ \text{rpm, } 2\ \text{minute})\) (Model Polos300 AWS), then the film is allowed to dry in air. ZnO films are sintered at \(400\ ^\circ\text{C}\) for 5 minute after deposition in air flow. Platinum contact electrodes are deposited by sputtering machine \((P = 100\ \text{Watt RF, } t = 2\ \text{minute})\) on the above of ZnO film’s surface. The final obtained of gas sensor device is tested by inserting it inside the homemade gas chamber and LPG is passed inside the chamber.

Characterization of ZnO and In-doped ZnO Nanopowders

X-ray diffraction patterns of doped and un-doped ZnO nanopowders are obtained using Schimadzu 7000 Diffractometer operating with Cu Kα1 radiation \((\lambda = 0.15406\ \text{nm})\) generated at 30 KV and 30 mA with scan rate of 2° min\(^{-1}\) for 20 values between 20° and 80°. ZnO:In nanopowders used for the realization of gas sensor device (MOS films, heaters and two platinum electrodes) were examined by (SEM) scanning electron microscopy (JEOL JSM 6360LA, Japan). The resistivity and the voltage of the gas sensor device are measured and subsequently, the sensitivity and voltage is plotted in contradiction of the studied gas temperature for all gases. After each measurement, the sensor is exposed to the atmospheric air by opening the chamber. The response of the gas sensor is defined as the ratio \((S = R_a/R_g)\), since \((R_a)\) is the resistance in dry air and \((R_g)\) is the resistance for the targeted gas for each temperature. The response and recovery times are determined as the times taken by the sensor to be realized 90 % of the total resistance change in the cases of adsorption and desorption, respectively [5].

Results and Discussion

Effect of in Doping on ZnO Characteristics

The scanning electron microscope images of pure ZnO and ZnO doped with 1%, 5%, and 10% Indium respectively are shown in Figure 1a, b, c, d. For pure ZnO, well-formed nanorods structures with an average length of about 5µm and a diameter of 300 nm predominates Figure 1a. With starting doping process with In doping ratio 1%, ZnO nanorods come to be shorter in length and the diameters increase as shown in Figure 1b. Increase in doping ratio of In to be 5% leads to the ZnO nanorods convert to elongated nanoparticles, then to spherical nanoparticles with 10% In doping ratio.
respectively Figure 1 c, d. It implies that In have an important effect on the crystallization.

**Figure 1.** *SEM Micrographs of (a) Pure ZnO, (b) ZnO:In=99:1, (c) ZnO:In=95:5, (d) ZnO:In=9:1*

All the diffraction peaks are indexed to be those of hexagonal wurtzite ZnO as shown in Figure 2 which agrees well with those given in relevant XRD database (JCPDS card No. 01-089-1397). Figure 2 indicates that, no characteristic peaks of any impurities are observed, which consider that In$^{3+}$ is consolidated in zinc oxide matrix by substituting Zn$^{2+}$. Moreover, there is a small difference in the patterns and intensities of the (100), (002) and (101) planes of various In doped ZnO nanopowders samples with different concentrations of In dopant Figure 2b, c, d. These results imply that the effect of the doping process on crystal structure and grain size of synthetic ZnO/In nanostructures is concentration-dependent.
**Figure 2.** X-ray Diffraction Pattern of Nanoparticles: (a) Pure ZnO, (b) ZnO:In=99:1, (c) ZnO:In=95:5, (d) ZnO:In=9:1

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**Gas Sensing Performance for Gas Sensor Devices**

The fabricated ZnO gas sensor is measured for the same concentration (100 ppm) of LPG. Moreover, the optimum doping ratios for different doped ZnO samples are applied as gas devices to determine the optimum dopant percentage and its suitable doping weight ratios for the highest sensitivity [6]. The films resistance is measured using half bridge method in air atmospheric at different temperatures.

For the LPG gas, it can be observed that, the sensitivity of ZnO thin films is increasing with increasing working temperature and reach a maximum value (from 150 to 250 °C, which is considered low working temperature) and then decreases with further increasing in working temperature as shown in Figure 3.

**Figure 3.** Sensitivity of ZnO Doped and Undoped Gas Sensor Measured as a Function of Temperature for LPG
The variation of the filament resistance is transmitted as a voltage variation. Figures 4 and 5 depict the output voltage of sensors for LPG gas with different loads. It is found that for increasing the load resistance to 1K Ω the voltage will decrease.

For In:ZnO films, the sensitivity values increase, comparing with pure ZnO. It is observed that, for the examined films, there are increasing in sensitivity with the increasing in In doping concentration in ZnO host. Actually, doping process is an important method to affect not only on the structural properties such as grains size, shape and/or morphological structure, but also the electrical properties. In the other words, gas sensing performance is improving in the case of doping process [7].

**Figure 4. Voltage of ZnO Doped and Undoped Gas Sensor Measured as a Function of Temperature for LPG with RL .5kΩ**

![Figure 4](image)

**Figure 5. Voltage of ZnO Doped and Undoped Gas Sensor Measured as a Function of Temperature for LPG with RL 1k**

![Figure 5](image)
It is clear that, the highest sensitivity for LPG is about 111% for fabricated ZnO doped 5% In at (210-220)°C, 88% for 1% In at (190-200) °C, 82% for 10 % In at (210-220)°C and 45% for pure ZnO at 200°C.

This process is resultant of increasing in the electron concentrations, which leads to increase in the conductivity of the ZnO/In gas sensor [8]. It is well known that, the gas response of the MOS gas sensors is mainly based on the interactions between a target gas and the surface of the MOS. So, for the greater surface area of the materials leads to the strong interaction between the adsorbed gases i.e., the gas response is higher [9]. In this work, it’s observed that from SEM images that for 5 % In, the elongated nanoparticles structures offers higher surface area to interact gas molecules. On the other hand, the heavy and bigger grains are observed for more concentrations (10 % In). The total surface area and grain borders are largest for 5 % In. The sensitivity could be improved by the significant change in the surface area with the largest number of adsorption–desorption sites [10].

The same behavior of gas sensing properties for Ce-doped ZnO thin-film sensors were reported in [11], since the gas sensing response value augmented gradually with the increase of Ce-doping ratio from 1% to 5%, however decreased gradually when the doping ratio increased than 5%. They found that CeO₂ phases congregating on the surface of the ZnO nanoparticles have positive effects and negative effects. Appropriate doping can improve sensing properties, but excess dopant decreases the gas sensing properties. Such kind of correlation between gas sensing response and doping percentage was also observed in the Fe-doped ZnO hierarchically porous nanosheets [12].

Conclusions

The goal of this research paper is to enhance the sensitivity of the ZnO gas sensor. This goal has been achieved by doping In with different concentration. The measured sensitivity proved that the best doping ratio of the fabricated gas sensor, which has a maximum sensitivity, is recorded at Zn/In = 95:5 is 111% For LPG. This concentration has a good voltage variation. By increasing the load resistance the voltage will decrease.

References


