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Synthesis of Dopant Zno Thin Films with Al Using Dip Coating for Gas Sensors

Abstract- *The sol-gel technique (dip coating method) used to synthesize pure Zinc Oxide and Aluminum doped Zinc Oxide thin films on glass substrate for gas sensing application. Zinc acetate dehydrate was used as source of Zinc ions. The influence of annealing temperature of pure ZnO thin films with three different temperatures (300,400,and 500) °C, Aluminum dopant concentration with two different concentration (3wt% and 5wt%) and annealing temperature for AZO thin films with three different temperatures (300,400,and 500) °C on gas sensing properties was studied. The results show that ZnO was to be sensitive toward CO gas and its sensitivity decrease with increase in annealing temperature of pure ZnO and (5wt.%) AZO thin films. It is found that the sensitivity of pure ZnO thin films decrease from 67% at 300 °C to 54% and 38% at 400 and 500 °C respectively. Likewise, for 5wt. % AZO thin film the sensitivity improved by increase the Aluminum dopant concentration with fixed annealing temperature 500 °C. It is found that the sensitivity increase form 49% to 57% when doped with Al at (3 wt. %) and (5 wt. %) respectively.*

Keywords- *AZO, Dip coating, Sol-Gel, ZnO.*

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1. Introduction

ZnO has more interest by researchers due to the wide diversity in use for its distinctive properties, which made it suitable for various applications. The zinc oxide (ZnO) is one of the important semiconductors with a large and direct energy gap of 3.37eV [1,2].

Many methods used to synthesis the ZnO thin films. Most these methods like spray pyrolysis, Physical vapor deposition (PVD), chemical vapor deposition (CVD), pulsed laser deposition (PLD), thermal evaporation, molecular beam epitaxy (MBE), and sol-gel technique [3]. Sol- gel method used to get Nano-structure of ZnO. Nowadays, the sol-gel methods with utilization of dip coating is widely used because of several merits such as, the easy control of chemical components, low cost techniques and low fabricating temperature [4,5].

ZnO can be doped by varies dopants such that Indium (In), Cobalt (Co), Iron (Fe), Antimony (Sn), Aluminum (Al) [6-8].

ZnO can be easy synthesis by wide different methods and by dopant it, one gets a good property for gas sensor applications [3].

ZnO:Al thin films have much application. One of these applications is gas sensors. The principle of gas sensors is working on the change of the electrical conductivity of sensing layer of thin films due to contact with the gas to be detect. The efficiency of the sensor depends on the interaction of the molecules of gas and the material of the thin films [9,10].

Many researchers have focused on gaseous sensors in terms of studying its properties and industrialization as a result of its many applications, including industrial and medical, as well as the use of gases in the atmosphere and its impact on the our environment .[11]

In 2008, V. Musat et al. studied the gas sensing properties of sol-gel ZnO thin films. The effect of withdrawal speed on gas sensitivity of the films has been studied. It was found that as the withdrawal speed increase both pore size and grain size is increased. The gas sensitivity increases as grain size decreases [12].

In 2013 R. S. Sabry. Studied the sensitivity of ZnO and AZO. It was found that the sensitivity increasing with Al doping [13].

In this article, pure ZnO thin films and other dopant with different Aluminum percentage had been prepared by dip coating on glass substrate. These thin films used as gas sensors to detected the gas CO .The effect of annealing temperature on the sensitivity also studied.

2. Experimental Work

The films were prepared over microscope glass substrate used sol-gel technique dip coating method. To prepare pure ZnO seed solution, zinc acetate dihydrate [Zn(CH3COO)2.2H2O] dissolved in a mixture of methanol and isopropanol (IPA) solvents, respectively. In order to dope the Aluminum element to ZnO, Aluminum chlorid-6-hydrate (AlCl3.6H2O) selected as a source material. (AlCl3.6H2O) with

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two different atomic percentage; (3wt.%, 5wt.%) and zinc acetate dehydrate added to, the mixture of methanol and IPA and stirred at room temperature for (30 min). The aged pure, and Al doped ZnO (with two different concentration 3wt.% and 5wt.%) solutions are deposited on glass substrates by using a dip coating technique. With a controlled withdrawal speed is (0.4 cm/s) and the deposition time (5 min) at room temperature. The dried was (150 °C) for (20 min) evaporate the solvent and eject organic residues. Then the films were annealed in a furnace under ambient air at different temperatures (300, 400, 500) °C for (2h) to get crystallized ZnO and AZO.

3. Experimental Apparatus

Gas Sensor Measurement; to measure the electrical properties, ohmic contacts is required (Electrodes deposition). The system of gas sensor was used to check the sensitivity of film for CO gas as shown in Figure 1. This system consists of the following parts: Vacuum pump, Connection tubes, Discharge sensor scale, and Pressure gauge. Figure 1 shows the chamber, which holds the sample and has many feed through, DC Power supply, Iron structure to fix the container of gas, and Electrical Resistance meter. The resistance of the film was measured in air (without CO gas). The gas was then pumped and the resistance of the sensor was recorded with time (every ten seconds).The resistance of the films measured in to two times, one in the air and the second in the presence, the gas .The difference of these reading is known as the sensitivity.

Figure 1: setup of Gas Sensing Test

4. Results and Discussion

The gas sensitivity measurement of ZnO thin film of CO gas was carried out at room temperature and it is calculated by measuring the differences in films resistance in both dry air (Ra) and in the presence of gas (Rg). The gas sensitivity (S) can found in terms of surface resistance change in the presence of gas with time is calculated by [14].

$$S\ (\%) = \left(\frac{Ra - Rg}{Ra}\right) * 100 \quad (1)$$

The gas sensitivity of ZnO thin film deposited on glass substrate with three different annealing temperatures as a function of exposure times showed in Figure 2. It can be seen that the gas sensitivity decreases with the increase in annealing temperature, it is decrease from (67%) at (300 ºC) to (54%) and (38%) at (400 and 500) ºC respectively. This is can explain it that the grain size increase with the rising of annealing temperature, the increase in grain size caused degradation of the gas sensitivity of the films also because of decrease the carrier concentration with increase the annealing temperature.

The gas sensitivity of such devices counts two effective factors, which are; grain size and the porosity of the material. These two factors play important role in the sensitivity. [12].

Doping ZnO thin films with Aluminum play important role in the improvement the sensitivity of the thin films to gases. Figure 3 shows the gas sensitivity for ZnO thin film annealed at (500 ºC) with different Aluminum dopant concentrations as a function of exposure times. It is clear from the figure that the gas sensitivity increase from (49%) to (57%) when doped with Al at (3 wt.%) and (5 wt.%) respectively, this is due to decrease in grain size of thin film. For the ZnO gas sensors, Al doping causes to increase in the oxygen vacancies and this leads to increase the sensitivity of the thin film.[15]

Figure (4) shows the gas sensitivity for AZO thin films doped with (5wt.%) Al and annealed at three different temperatures as a function of exposure times. From the figure it is observed that the gas sensitivity decrease with increase in annealing temperature. The gas sensitivity decrease from (74%) at (300 ºC) to (65%) and (57%) at (400 and 500) ºC respectively. The decrease in gas sensitivity attributed to the increase in grain size also decrease in carrier concentration of the AZO thin film.

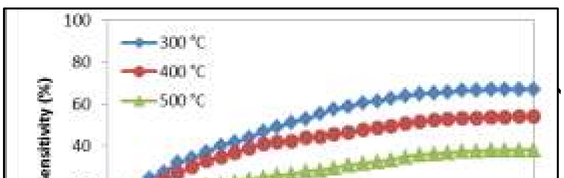

Figure 2: The gas sensitivity of ZnO thin films for CO gas as a function of exposure time with different annealing temperatures

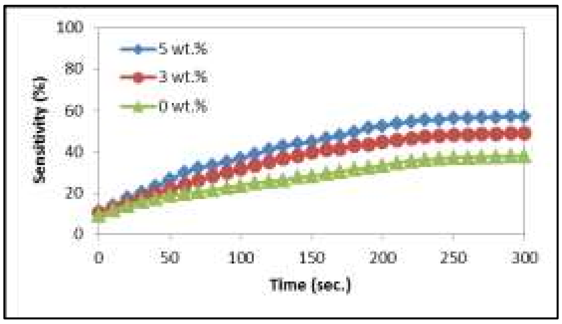

Figure 3: The gas sensitivity of AZO thin films for Co gas as a function of exposure time annealed at (500°C) with different Aluminum concentrations

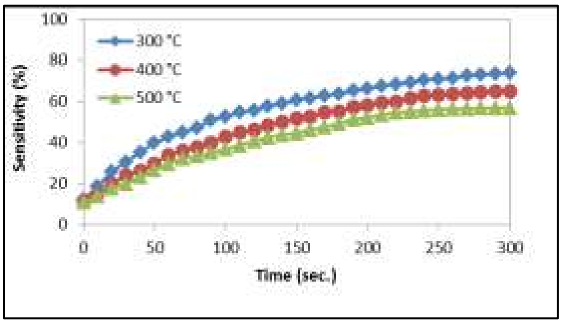

Figure 4: The gas sensitivity of (5 wt.%) AZO thin films for Co gas as a function of exposure time with different annealing temperatures.

4. Conclusion

ZnO thin films can be reliable in application in gas sensor for CO gas at room temperature and their sensitivity decrease with increase annealing temperature, and increase with respect to the concentration of Al dopant due to increase in grain size. This result makes the doping with Al an important parameter to improve the sensitivity of the ZnO thin film. The highest sensitivity was found with doping Al at annealing temperature 300 ºC.

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