

Carbon monoxide gas sensing using zinc oxide film deposited by spray pyrolysis

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Abstract. This study was aimed to determine the carbon monoxide (CO) gas sensing ability of zinc oxide (ZnO) film fabricated by spray pyrolysis on glass substrate heated at 300°C using 0.2 M zinc acetate precursor solution. The temperature of the precursor solution was maintained at room temperature. Carbon monoxide gas was synthesized by mixing the required amount of formic acid and excess sulfuric acid in the ratio of 1:6 to produce CO gas concentrations of 100, 200, 300, 400, and 500 parts per million (ppm) v/v. There were five trials for each concentration. The films produced exhibited good sensor characteristics such as high linearity in current voltage relationship and voltage response versus concentration. Electrical characterization using the four-point probe showed a linear relationship between current and voltage with resistivity of 0.49 ohm-cm and R² value of 0.994. The zinc oxide film exhibited a sensitivity of 0.19 Volt per 100 ppm of CO gas and linearity R² value of 0.993.

1. Introduction

Carbon monoxide (CO) is highly toxic and the danger lies in its being tasteless, odourless, and colourless so that it is not easily detectable. CO poisoning can be classified as acute, chronic or occultic. Single exposure to large doses of CO gas can cause acute CO poisoning. Repeated exposure to low levels of CO for an extended period of time cause chronic poisoning in which the harmful effects are manifested at a later time. Occultic poisoning can either be acute or chronic but the cause is misdiagnosed [1]. Death can occur if the concentration inhaled by a person is 35 ppm for over 8 hours as ascribed by the United States National Institute of Occupational Safety and Health (NIOSH). CO combines with haemoglobin to form carboxyhaemoglobin reducing the total capacity of the blood to carry oxygen [2]. It was reported by [3] that pregnant women, children, infants and individuals lost their lives due to air pollution caused by this deadly gas in Lagos, Nigeria. Since low concentrations are equally dangerous to high levels it is important to have extremely sensitive sensors for monitoring. Human activities account for artificial sources of CO (60%) in the environment and the rest are present naturally (40%) [1]. Common sources of CO include motor vehicles, household fires, and appliances that use carbon based fuels[2,4] Other exogenous sources of CO include as car exhaust fumes, furnaces, gas-powered engines, home water heaters, paint removers containing methylene chloride, pool heaters, smoke from all types of fire, tobacco smoke, and wood stoves [5].



Zinc oxide (ZnO) is an n-type metal oxide semiconductor (MOS) that has important electronic, chemical and physical characteristics making it a well-known commercial sensor because of the sensitivity of its properties to variations in its chemical environment. It has a high chemical sensitivity to adsorbed gases making it useful as a gas sensor [6,7].

When gas molecules interact with the semiconductor surface, properties such as resistance, conductivity and surface potential are affected. Oxygen molecules that are adsorbed on ZnO surface bind to its vacancy sites, extracting or trapping electrons from the conduction band (E_c). The electrons are conducted to the surface and become strongly attached as charged oxygen anions. This results to an increase in the surface resistance and the formation of a space-charge layer. When reducing gases such as CO react with the adsorbed oxygen CO_2 is produced with a consequent release of electrons back to the conduction and increase in conductivity of the semiconductor [8].

There are many different methods of depositing semiconductor films such as metalorganic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), liquid phase epitaxy (LPE), sol-gel processing, spray pyrolysis, electrophoretic deposition (EPD) and successive ionic layer adhesion and reaction [9].

Spray pyrolysis is a technique in preparing thin and thick films, ceramic coatings, and powders that is simple and relatively cost-effective. It does not require high-quality substrates or chemicals. Typical spray pyrolysis equipment consists of an atomizer, precursor solution, substrate heater, and temperature controller. Spray parameters that affect the film quality include substrate temperature, precursor solution composition and temperature, and aerosol delivery [10]. Studies showed that zinc oxide with hexagonal wurtzite-type structure can be produced by spray pyrolysis on substrates with temperatures above 500 K [11,12]. Zinc acetate is a good substitute for tin oxide (SnO_2) and is the preferred precursor because of its high vapor pressure [11,13,14,15]. Krunk and Mellikov demonstrated that for solar cell applications it is preferable to use growth temperatures of 625-675 K, indium doping levels of 1-1.5 at.% and precursor concentrations of 0.1-0.2 mol/li to produce ZnO films with good optical and structural qualities [9].

2. Methodology

2.1. Preparation of materials

Glass substrates were prepared with dimensions of 2.0 cm by 0.4 cm and ultrasonically cleaned by ethanol for 15 minutes and dried by air. Commercially available plastic perfume atomizers (60 mL) were cleaned with soap and water and washed with distilled water then ethanol. An improvised enclosure made of card board was made with dimensions of 29 cm x 40.5 cm x 25 cm for the spray pyrolysis set-up.

Zinc acetate dihydrate powder was mixed with distilled water in a concentration of 0.2 M. The solution was stirred using a magnetic stirrer for 60 minutes and then transferred to an atomizer.

2.2. Film fabrication

The spray pyrolysis set up consisted of an atomizer, zinc acetate dihydrate solution, and substrate heater maintained at 300°C. The solution maintained at room temperature was sprayed intermittently on the heated glass substrate using an atomizer for a total duration of 30 minutes. There was an interval of five seconds between successive sprays. Three replications for each trial was made totalling fifteen films for the five different gas concentrations to be tested. The films were annealed at 300°C after deposition.

2.3. Film characterization

The I-V characteristics of the films were determined using the four-point probe while the morphology of the film was examined by scanning atomic force microscopy.

2.4. Gas sensing

The sensor was connected as one arm of a Wheatstone bridge supplied with 5 V DC power to test the gas response of the film sensor. The sensor was placed inside an airtight container of known volume filled with varying amounts of carbon monoxide. The concentrations used were 100, 200, 300, 400, and 500 ppm v/v. which were generated by mixing the corresponding amounts of formic acid and sulphuric acid in a beaker inside the gas chamber using a magnetic stirrer. Three trials were conducted per concentration.

3. Data and Results

The atomic force microscopy (AFM) image of the zinc oxide film is shown in Figure 1-A. The histogram of the AFM image showed high variations on vertical dimensions suggesting elongated structure that is consistent with nanorod-like elongated structures. The structure consisted of rod-like structures as well as nanowires. The large surface area offered by the nanorods and nanowires is beneficial to the function of the film sensor since gas sensing is a surface phenomenon. This result is supported by previous studies that showed the formation of nanorods when the substrate temperature is above 500 K [8,9]. The substrate temperature used in this study was 573 K.

Electrical characterization using the four-point probe showed a linear relationship between current and voltage with resistivity of 0.49 ohm-cm and R^2 value of 0.994, as shown in Figure 1-B

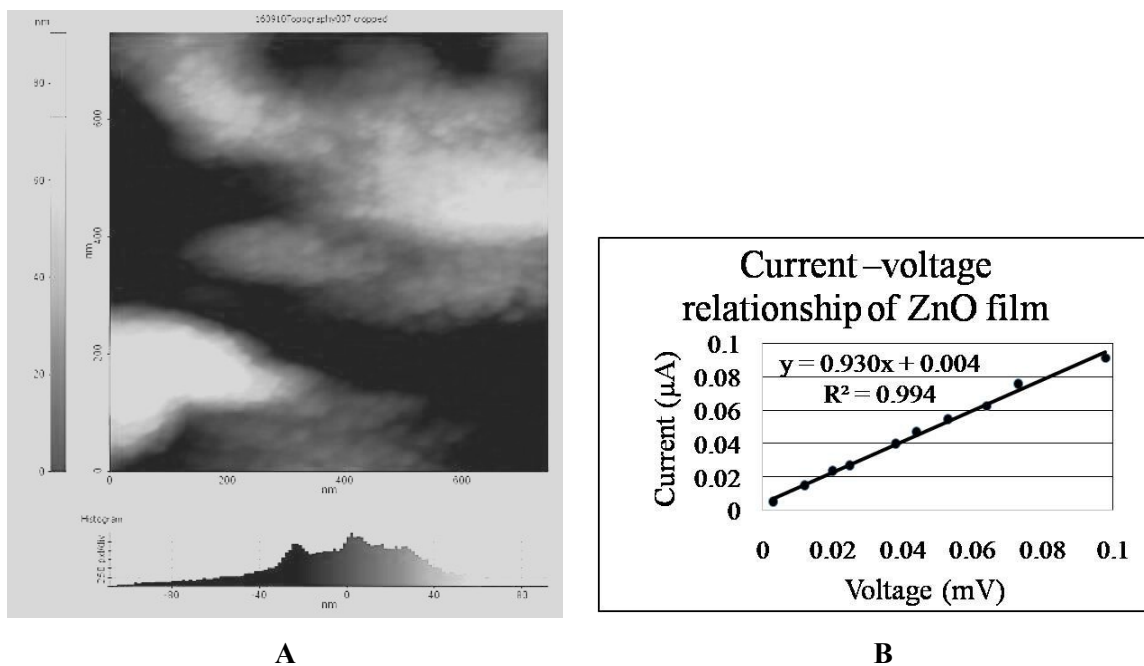


Figure 1. A. Atomic microscopy (AFM) image of the zinc oxide film showing nanorods and nanowires at 10k (a) and 20k magnification. **B.** IV curve of the zinc oxide film showing linear relationship between current and voltage.

Figure 2 shows the graph of voltage response of the ZnO film with time. The maximum change in voltage output of the film was observed at 200 seconds after which the gas was released. The vertical shift after 200 seconds indicates a fast recovery of the film at 90% followed by a slower recovery (90 to 100%) up to 600 seconds. The voltage response was calculated from this graph using the difference between the initial voltage reading before exposure to gas of the film and the lowest final voltage reading

Figure 3 shows the voltage response of the ZnO film sensor to different carbon monoxide concentrations. Each data point is the average of the voltage response from each of the three replicates.

Results showed a sensitivity of 0.19 volts per 100 ppm of CO concentration with high linearity and R^2 value of 0.994.

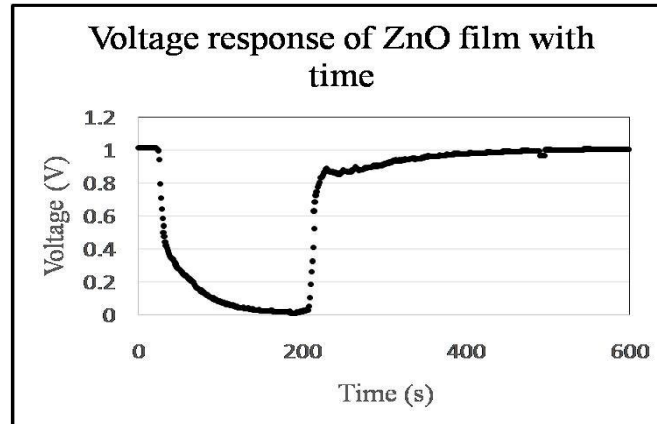


Figure 2. Graph of voltage response of the ZnO film with time with maximum voltage output at 200 seconds after which the gas was released. The vertical shift after 200 seconds indicates a fast 90% recovery of the film followed by a slower recovery (90 to 100%) up to 600 seconds.

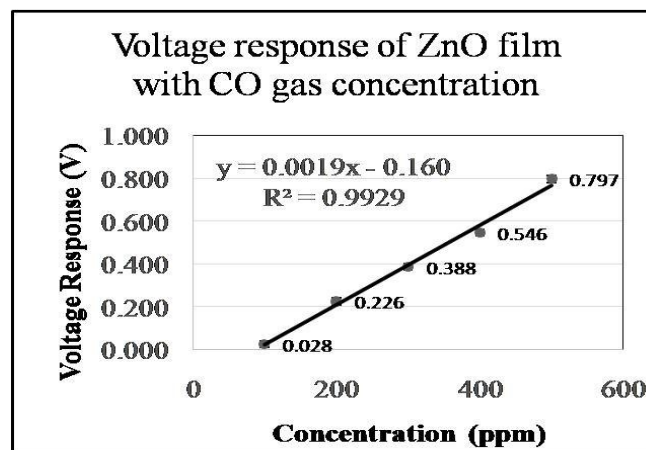


Figure 3. Voltage response of the ZnO film with concentration in ppm (v/v).

4. Conclusion

This study was able to show that good quality zinc oxide thin films can be produced using low cost method and materials. The 0.2 M Zinc acetate precursor solution at room temperature was sprayed intermittently for 30 seconds on a 300°C glass substrate with an interval of five seconds between sprays. The films produced exhibited good sensor characteristics such as high linearity in current voltage relationship and voltage response versus concentration. Electrical characterization using the four-point probe showed a linear relationship between current and voltage with resistivity of 0.49 ohm-cm and R^2 value of 0.994. The zinc oxide film exhibited a sensitivity of 0.19 Volt per 100 ppm of CO gas and R^2 value of 0.993. This would be beneficial to the production of low-cost sensor instruments with cheap replaceable sensors. It is also recommended to test the reusability of the sensor produced by the pyrolysis method and the repeatability of the results.

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References

- [1] Wright J 2002 Chronic and occult carbon monoxide poisoning: we don't know what we're missing *Emerg Med J.* **19** 386–390
- [2] Meredith T and Vale A 1988 Carbon monoxide poisoning *British Med. J.* 77-79
- [3] John K S and Feyisayo K 2013 Air pollution by carbon monoxide poisonous gas (CO) in Lagos area Southwestern Nigeria *Atmospheric and Climate Sciences* **3** 510-514
- [4] Myers R, Linberg S, Cowley R 1979 Carbon monoxide poisoning: The injury and its treatment. *JACEP* **8** 479-484
- [5] Varon J and Marik Paul 1997 Carbon monoxide poisoning *The Internal Journal of Emergency and Intensive Care Medicine* **1 N2**: <http://www.ispub.com/journals/IJEICM/Vol1N2/CO.htm>
- [6] Weng J ,et al. 2004 *Thin Solid Films* **478** 25
- [7] Wellings J, Chaure N, Heavens S, and Dharmadas I 2008 *Thin Solid Films* **516** 3893
- [8] Chakraborty S, Sen A and Maiti H S 2006 *Sensors and Actuators B* **115** 610–613
- [9] Hsu C, Chen K, Tsai T and Hsueh T 2013 *Sensors and Actuators B* **182** 190
- [10] Perednis D and Gauckler L J 2005 Thin film deposition using spray pyrolysis *J. of Electroceramics* **14** 103-111
- [11] Krunk M and Enn E 1995 Zinc oxide thin films by the spray pyrolysis method *Thin Solid Films* **270** 33-36
- [12] Hassan H S, Kashyout A B, Morsi I, and Nasser A A A 2014 Synthesis, characterization and fabrication of gas sensor devices using ZnO and ZnO:In Beni-Suef Uni. *J. of Basic and App. Sci.* **3** 216-221
- [13] Caillaud F, Smithand A, and Baumard J F 1990 *J. Eur. Ceram. Sm.* **6** 313
- [14] Ayouchi R, F. Martin, Leinena D, and Ramos-Barrado J R 2003 Growth of pure ZnO thin films prepared by chemical spray pyrolysis on silicon *J. of Crystal Growth* **247** 497–504
- [15] Nunes P, Fernandes B, Fortunato E, Vilarinho P, and Martins R 1999 Performances presented by zinc oxide thin films deposited by spray pyrolysis *Thin Solid Films* **337** 176-179