A Modified Zinc Oxide (ZnO) gas sensor approach to detect oxidizing gases

Lungisani S Phakathi, Sanele S Gumede and Betty Kibirige

Department of Physics and Engeneering, University of Zululand, kwaDlangezwa campus, kwaZulu natal, South Africa.

E-mail: `lungisani.sipho.phakathi@cern.ch`

Abstract. Selective detection of gases such as nitrogen dioxide (NO_2), carbon monoxide (CO), carbon dioxide (CO_2), and various volatile organic components is necessary for air quality monitoring and safety. There are several metal oxide gas sensor (MOGS), but the focus of this study was Zinc Oxide (ZnO); an n-type MOGS. NO_2, an oxidising gas was the target gas. The aim of this study was to establish the possible enhancement of a gas sensor selectivity by the introduction of signal conditioning electronics circuitry such as the Wheatstone bridge in tandem with an operation amplifier circuit. Exposing electronics enhanced ZnO MOGS system to NO_2 resulted in a increasing negative voltage output between 0 and – 3.5 V. This range of voltages is sufficient to run a micro-controller, with the assumption that a reducing gas would result in a positively increasing voltage, a micro-controller could be conditioned to select between an oxidising and a reducing gas.

1. Introduction

When a Metal Oxide Gas Sensor (MOGS) is exposed to gaseous chemicals its resistivity changes with concentration of the gas. ZnO is an n-type MOSG due to the fermi level is near the conductive band, with a band gap of 3.37 eV and that allows for it to work under chemoresistance principle and NO_2 is an oxidising gas of interest. When ZnO is exposed to NO_2 gas the following chemical reactions take place:

$$\mathrm{N}O_{2(gas)} + e^-_{(surface)} \longrightarrow NO^-_{2(adsorbed)} \tag{1}$$

$$\mathrm{N}O_{2(gas)} + O^-_{2(adsorbed)} + 2e^-_{(surface)} \longrightarrow NO^-_{2(adsorbed)} + 2O^-_{(adsorbed)} \tag{2}$$

This shows that electrons are taken away from the surface that leads to an increased resistance of the ZnO MOGS. On the other hand, when a reducing gas is introduced to the surface of the ZnO gas sensor, electrons are introduced in the conduction band of ZnO, reducing the resistance of ZnO [1]. For this project, a Wheatstone bridge was designed and introduced to balance with no gas present. The Wheatstone bridge is sensitive to small resistance changes. Thus by using a Wheatstone bridge, changes in resistance of the MOGS due to the gaseous environment can be easily measured quantitatively. The Wheatstone bridge equation (3) was captured in excel to allow comparison between simulated and theoretical results.

$$V_{out} = \left(\frac{1}{1 + \frac{R_2}{R_1}} - \frac{1}{1 + \frac{R_3}{R_4}} \right) \tag{3}$$

A gas sensor is a device which receives a chemical signal and responds by converting it into an electrical signal. A gas sensor is a mandatory tool that is used to identify a specific task assigned to it [1]. In this experiment the gas sensor was a semiconductor (ZnO) device that would be used to senses toxic gases in industries and general working environments. The aim was not to measure the resistance of the gas sensor in the presence of the targeted gas, but rather measure the output voltage of the gas sensing system.

1.1. Zinc Oxide as a gas sensor

Over the past decade, scientists have made important improvements in the quality of ZnO as an electronic material in its own right. The detection of a specific gas is enabled by using semiconductor sensors that are selective too particular chemical species [2]. The existing sensors that have been produced give a response to a mixture of gases. This means that such sensors are not selective enough to a specific chemical species. In order to solve this problem, an array of sensors which are able to simultaneously detect different gaseous chemical species was introduced. This arrangement made it possible to sense a variety of gaseous chemical species by giving the correlation among a large number of sensor outputs [3].

A ZnO is a kind of material that is widely used in electronic and opto-electronic applications because of its abundance, non-toxicity and low costs[4]. ZnO is a well-known material that is a II-VI compound semiconductor with a wide band gap energy of $3.37eV$ [5]. The response of the ZnO gas sensor towards some targeted gases may be upgraded by doping, reducing grain size or changing the temperature and humidity [6]. The crucial characteristic that manufacturers need in a gas sensor is for it to be selective with respect to the type of the targeted gas that is oxidizing or reducing [7].

The metal oxide gas sensor works on a chemoresistance principle. When the gas molecules interact with a metal oxide surface, it acts as either an acceptor or donor. The resistivity or electrical conductivity of a metal oxide thin film changes as it interacts with the target gas. The resistivity of the metal oxide semiconducting thin film depends on the majority carrier in the film. This happens if it is oxidized or reduced at ambient temperature [8]. The gas molecules undergo Reduction-Oxidation (REDOX) reactions. A surface adsorption site ensures correct interaction of gas molecules with the material. The adsorption can be observed by tempering with temperature. Below 200 ℃, oxygen can accept one electron and above it can accept two, as shown by equations (4) and (5) [9]. In the case of a n-type sensor, the surface gets depleted with electrons by presence of any other ions such as oxygen and upon exposure to a target gas (NO_2), these species reacts with the gas molecules to reverse back electron to the conduction band of the surface, resulting in decreasing conductivity [10].

$$\mathrm{O}_{2(gas)} + e^-_{(surface)} \Longleftrightarrow O^-_{2(adsorbed)} \tag{4}$$

$$\mathrm{O}_{2(gas)} + 2e^-_{(surface)} \Longleftrightarrow 2O^-_{(adsorbed)} \tag{5}$$

1.2. Synthesis of ZnO MOGS thin films

There are many methods used to deposit ZnO for different applications. The chemical bath method is the preferred method because it is simple to follow, requires low temperatures and low cost of deposition equipment. Chemical bathing [11] is a method used to deposit thin films and nanomaterials in a large area continuous deposition. In this paper, thin films of ZnO have been deposited on a silica glass substrate using the chemical bath method. Two aspects were investigated that is the chemical composition, and the morphology of the film as well as the energy band gap before introducing it into the gas sensing environment.

1.3. Description of existing gas chamber

The gas testing chamber can endure extremely high temperatures. The temperature was varied in order to establish its effect on the sensitivity of the sensor to the test gas. The test chamber made from brass has a transparent lid to allow for easy visual monitoring of all connections.

The gas testing chamber is equipped with a heating stage that is capable of heating the sample to a desired temperature, which varied between 100-400 ℃. The heating is with six 33 kΩ resistors with a power rating of $10W$ and a thermocouple to measure the temperature of the stage. The stage temperature is controlled by adjusting the supply voltage from a power supply.

It has two inlet pipes for the introduction of gases, that is the test gas and the flushing gas. It has one pipe outlet that removes the gas from the chamber. The outlet pipe is immersed into water to reduce possibilities of explosion.

The stage is made to accommodate the sample for its gas sensing testing. A sample was placed on the substrate that has silver contact with a copper wire connected to a Tru-RMS multi-meter used to measure the test gas effect on the resistance of the samples.

1.4. Proposed concept

The objective of this study is to modify an existing *ZnO* gas chamber sensing device [12]. An output voltage in a range of 0 to 5 V is required to run a micro-controller that monitors the test gas as it is introduced in the gas sensing device.

1.5. The Wheatstone bridge circuit

The Wheatstone bridge circuit diagram is shown below. The Wheatstone bridge was designed

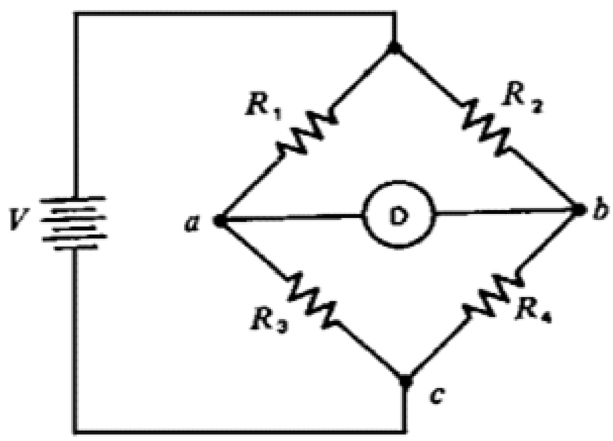

Figure 1. The Wheatstone bridge circuit.

to balance using the gas sensor resistance reading obtained when it is in the air environment. The purpose of using Wheatstone bridge, was to convert the changing in sensor resistance into a changing output voltage of the whole simulation. To monitor the gas inside and outside of the chamber two gas sensors are used and placed at the R_1 and R_4, as in figure 1. This serves as the normalising resistance and at this resistance value, the output voltage of the bridge is zero.

For an oxidising gas, the ZnO gas sensor resistance is at a maximum when it is exposed to air. The resistance decreases to a steady state minimum when an oxidising gas is introduced.

2. Design and simulation using PSpice

The Personal Simulation program with integrated circuit emphasis (PSpice) allows a user to capture a circuit diagram, simulate and analyse possible outcomes of the circuit. It has the power to calculate complex node voltages and branch currents across the captured design, allowing a user to generate relevant data for further analysis. The connection is done in port a and b as shown by figure 1 of the Wheatstone bridge and the circuit with an Operation Amplifier (OpAmp) which amplifies measured voltage is shown in figure 2 was captured in PSpice. The

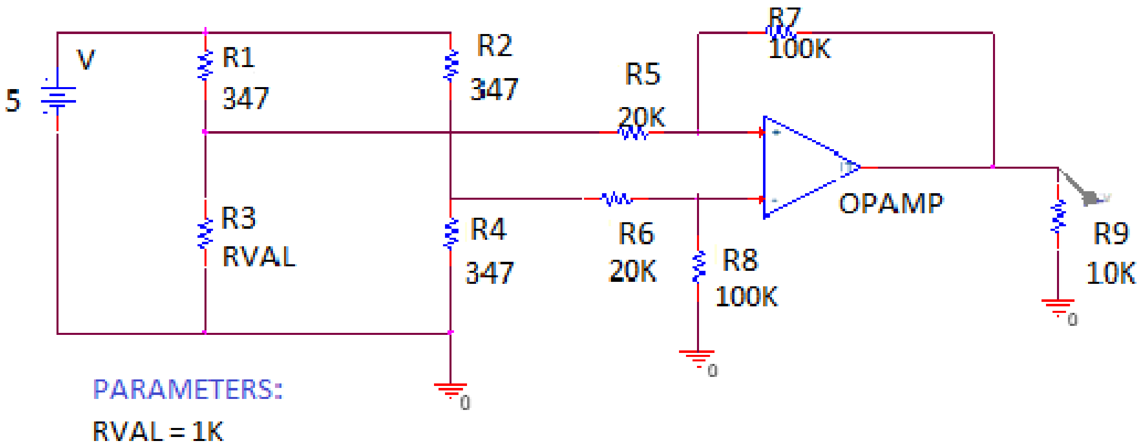

Figure 2. The schematic diagram of proposed concept in PSpice.

OpAmp at the output port of the Wheatstone bridge measures the output voltage from the bridge and amplify it to a voltage suitable for micro-controllers. The Wheatstone bridge was designed to be in balance when the gas sensor is not exposed to the target gas. Resistor R1 and R3 represent the sensor resistance in air and in a gas chamber respectively. Resistor R2 and R4 acts as a normalising gas sensor, chosen to be equal to R1 in contemplation of giving zero output voltage when there is no gas present in the chamber. In the circuity of figure 2, the ratio $\frac{R_7}{R_5}$ or $\frac{R_8}{R_6}$ determines the amplification factor of the amplifier.

$$V_{out_{OpAmp}} = V_{out}\left(\frac{R_7}{R_5}\right) \tag{6}$$

2.1. Sensor resistance and the balancing of the Wheatstone bridge

Using the results presented by Shichi Seto et al. [7] on the Mathematical modelling of a semiconductor gas sensor, the change in gas sensing resistance was used to test the proposed concept. At 350 °C, the variable resistor (RVAL), that represented the sensor, was varied between 625 and 347 Ω in steps of 5 Ω in the absence and presence of the targeted gas respectively.

3. Results and discussion

Figure 3 shows an Excel comparison of the voltage results obtained from the PSpice simulations across the output resistance R9 in figure 2 and those obtained theoretically using mathematical models of equation 6. The graph shows a negative increase of voltage as the gas enters the

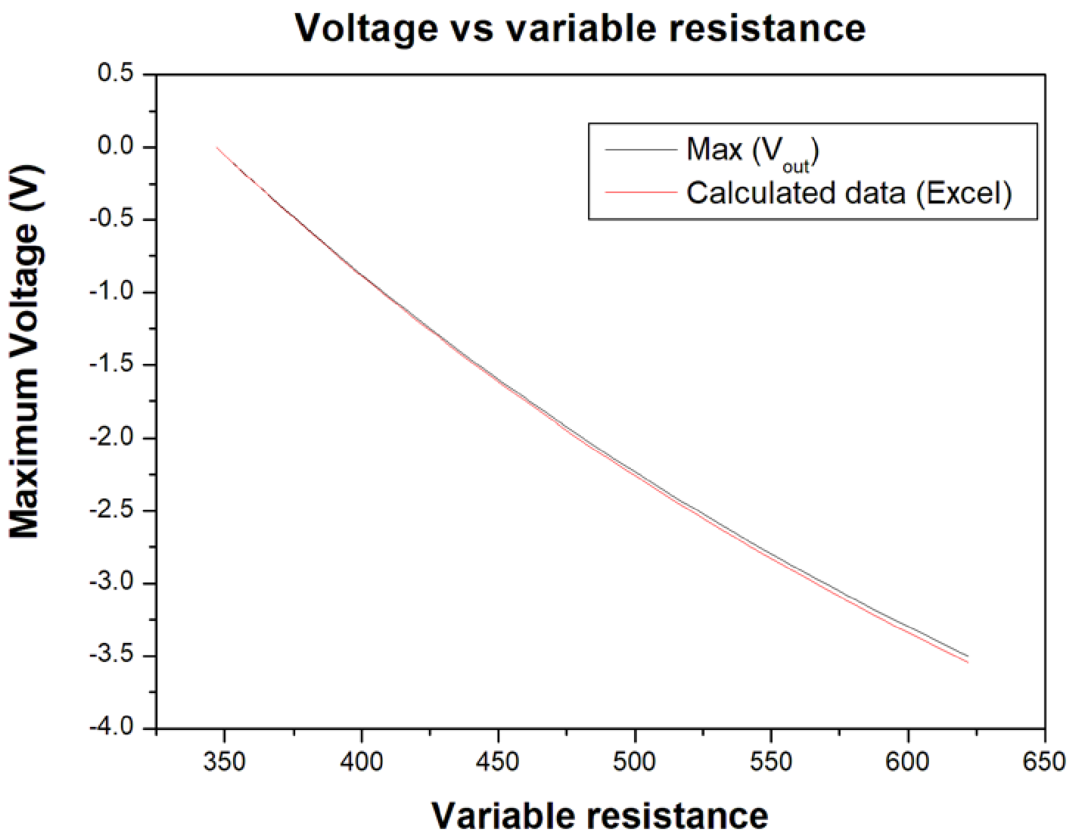

Figure 3. Readings of the maximum output voltage in the variable resistor as influenced by oxidizing gas. The graph shows the negative increase as the NO_2 gas enters the chamber.

chamber. The results clarifies that the oxidizing gas increases the resistivity of ZnO reducing the output voltage of the system.
The output voltage magnitude lies in the range: 0.0 to -3.5 V and is sufficient as an input to a micro-controller. The overlapping of the two curves all the way through the same path, clarifies that the simulated results using the PSpice environment agree well with the calculated results. As mentioned in the introduction, when a reducing gas is introduced to the surface of the ZnO gas sensor, electrons are introduced in the conduction band of ZnO. Therefore, the assumption for the presence of a reducing gas would be a graph showing a positive increase in voltage as the gas enters the chamber.

4. Conclusion

The designed circuit was successful in providing the required voltage that can be used as input to the micro-controller, that requires a voltage between 0.0 and -3.5 V. Results show the correlation with theory of an oxidizing gas leading to a negative output voltage from the ZnO sensor for an oxidizing gas. Results from simulated circuit in PSpice agree with the result from calculated result. This range of voltages is sufficient to run a micro-controller, with the assumption that a reducing gas would result in a positively increasing voltage, a micro-controller could be conditioned to select between an oxidising and a reducing gas.

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