High Sensitive O_2 Transducer by Gallium Oxide Thin Film

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***Abstract*-** This thesis is mainly to study the oxygen sensing characteristics of gallium metal oxide film at high temperature, and to analyze the oxygen sensing at temperatures above 600°C. First, the gallium oxide thin film is grown on the silicon substrate by sputtering, and the film quality and the boundary particle size are determined by different sputtering conditions, and the film structure is analyzed by atomic force microscopy. Finally, using this intrinsic and variable resistance characteristic of a gallium oxide film under oxygen, a simple Wheatstone bridge circuit was designed to successfully complete an oxygen voltage sensing transducer.

Index Terms- transducer, gallium oxide, oxygen sensor, Wheatstone bridge

I. INTRODUCTION

The development of the automobile industry has brought people a more convenient lifestyle, but relatively embarrassing is the problem of energy shortage and environmental pollution. The most critical component in controlling this big problem in automotive components is the O_2 sensor. In terms of energy conservation, the main purpose of the oxygen sensor is to prevent the mixed gas from being too rich or too lean, causing some unburned gasoline to accumulate in the catalytic converter, causing the temperature to be too high and burning the catalyst. When the mixture is too rich, the oxygen sensor transmits the excessive signal to the engine control module (ECM) to reduce the fuel injection time of the injector and reduce the injection amount of the gasoline, so as to achieve fuel saving. Up to date, Gallium oxide (Ga_2O_3) is one of the most recent potential oxides and can be used as a material in metal-oxide gas sensors. It has a high temperature sensing property, which is caused by oxygen sensing due to defects in the crystal lattice in the crystal lattice. In order to obtain an oxygen sensor with high performance, the characteristics of easy to manufacture with gallium oxide (Ga_2O_3), stable characteristics, fast reaction speed and low price have been used. During film growth, the target is sputtered and oxidized by sputtering. Gallium material and then a new high-temperature oxygen sensor of platinum-gallium-platinum sandwich structure (Pt-Ga_2O_3-Pt sandwich), which is expected to be applied to high-temperature industrial applications such as steam, in order to achieve the purpose of fuel economy and environmental safety and environmental protection. Typically, the oxygen induction mechanism can be explained as follows: the oxygen molecules adsorbed by the metal oxide at a high temperature and converted into ionized molecules or ionized atoms, that is, or caused to extract electrons from the conduction band. [1] Then, the surface state is modified by reducing the vicinity of the carrier and the formed semiconductor interface of the depletion region. While the oxidizing gas occupies the sensor surface, more oxygen will adsorb on the surface and then attract more electrons from the conduction band. The result of this surface conductivity reduction of this reaction can be written as given by the following equation:

$$O_2(gas) \Leftrightarrow O_2(ads) \qquad (1)$$

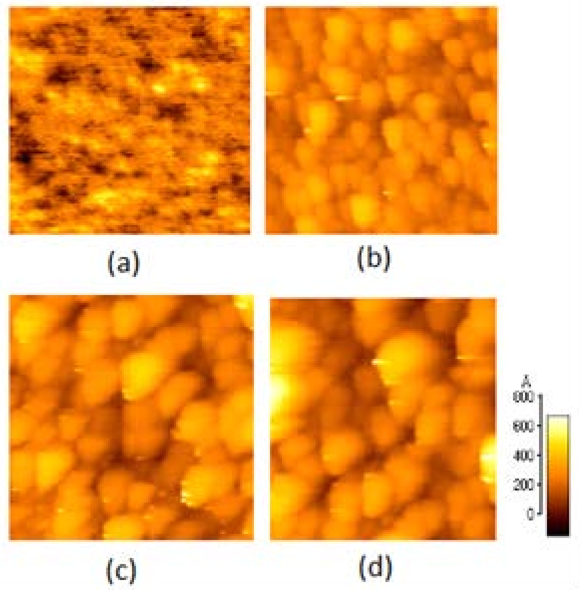
$$e^- + O_2(ads) \Leftrightarrow O_2^-(ads) \qquad (2)$$

$$e^- + \frac{1}{2}O_2 \Leftrightarrow O_2^-(ads) \qquad (3)$$

Therefore, the amorphous gallium oxide film can be used as a good gas sensor with insufficient oxygen. [2-3] Improved conductivity, which can be thought of as the presence of many unoccupied bonds and is caused by oxygen vacancies.

II. EXPERIMENTAL

Based on the physical understanding of the principle of oxygen sensors, etching the gallium oxide sandwich structure, suggesting that there may be more unoccupied bonds and high oxygen sensitivity is expected in this study. In Fig. 1, the AFM image shows the grain surface of the gallium oxide film in the area range of 1.2um x 1.2um under the sputtering pressure of different powder targets, that is, the pressure is 5Pa, 4Pa, 3Pa, 2Pa film surface condition. It has been found experimentally that the crystal faces of films deposited at low sputtering pressures have a larger grain size than when subjected to high sputtering pressures. Therefore, the average grain size observed for the deposited film was gradually increased from Figs. 1(a) to (d). At the same time, from the experiment, the film deposited after the thermal annealing, while increasing the temperature of the substrate also increases the grain surface size.



(a) (b)
(c) (d)

Figure 1: AFM gallium oxide film deposition pattern at pressures of (a) 5 (b) 4 (c) 3 and (d)2Pa, respectively

Figure 2,3 shows the corresponding current-voltage (I-V) characteristics. The electrical properties of the platinum-gallium oxide-platinum structure is measured at room temperature and 20% O_2 at a temperature of 700^0C. The structure of the element is a metal-oxide layer. Metal-oxide-metal (MSM), the current-voltage curve is a graph similar to the diode. The current-voltage curve is symmetrical under positive and negative polarity, and there is a corresponding turn-on voltage under forward bias (turn-on voltage) are 1V and 1.3V respectively. The relatively high turn-on voltage is mainly attributed to introduction of oxygen. The most important reason for the high turn-on voltage when containing condition at 20% oxygen is due to oxygen vacancy caused by the induced resistance to rise, so the behavior is different from those at 30% and 40% O_2 concentration. The current-voltage graphs are shown in Figures 4, 5. The corresponding turn-on voltages are 1.45V and 1.75V, respectively. The four diode idealization factors under forward bias are 1.3, 1.8. 1.85, 2.15, respectively. [2-3]

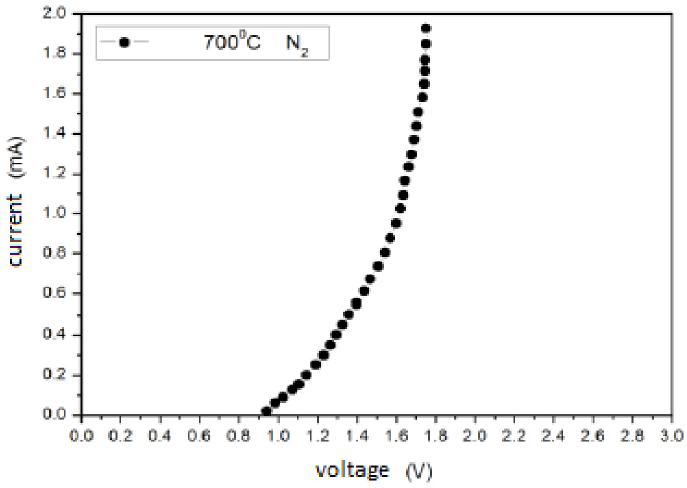


Figure 2: Current-voltage graph of platinum-gallium oxide-platinum under N_2 at temperature = 700^0C

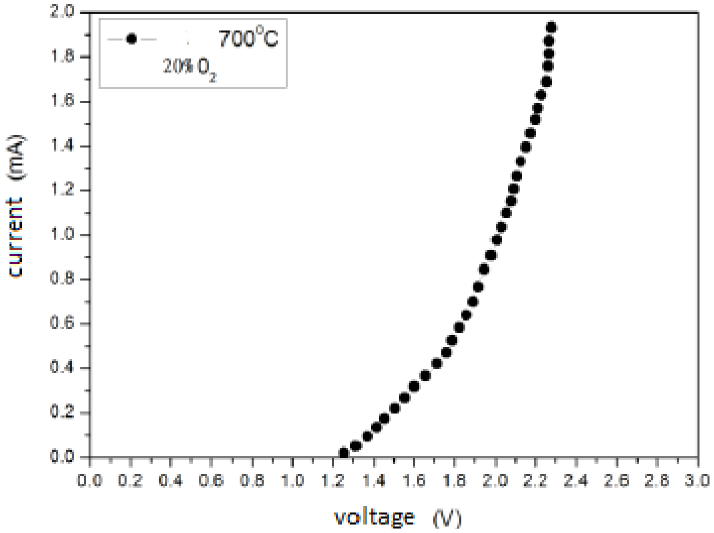


Figure 3: Current-voltage graph of platinum-gallium oxide-platinum at 20% O_2 at temperature = 700^0C

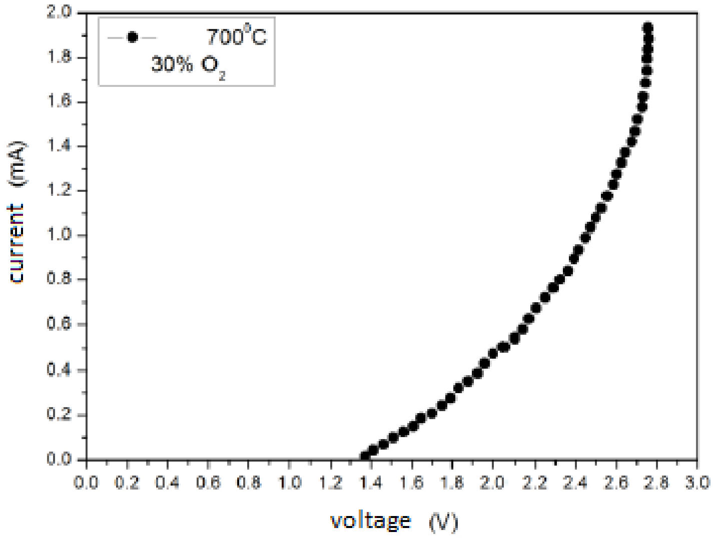


Figure 4: Current-voltage graph of platinum-gallium oxide-platinum at 30% O_2, temperature = 700^0C

For a diode characteristic, its behavior is shown as eq. (4), where V_D is the diode voltage, V_T the thermal voltage, I_S the saturation current, and n is the ideal factor. The closer n is to the nearest one, the closer it is to the ideal diode.
where

$$V_D \approx n \cdot V_T \cdot \ln 10 \cdot \log_{10}\left(\frac{I}{I_S}\right) \qquad (4)$$

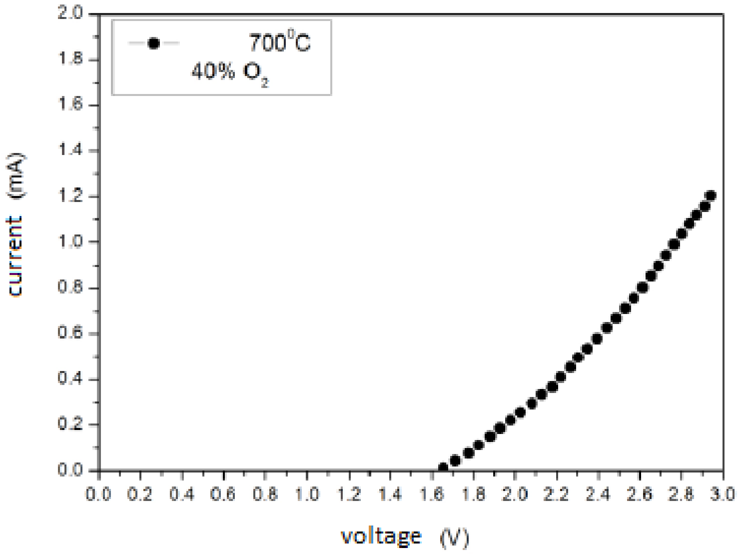


Figure 5: Current-voltage graph of platinum-gallium oxide-platinum at 40% O_2 at temperature = 700^0C

III. RESULTS AND DISCUSSION

This surface-etched oxygen sensor has a typical dynamic response curve as shown in Fig. 6 under an O_2 gas mixture of 0% and 35%. At the same time, increasing the concentration will increase the sensing resistance, because the electrons are in the phenomenon of electrical conduction. Contrary to this, when the concentration is lowered, a decrease in the sense resistance occurs, which means that the electrical conduction is caused by the formation of oxygen vacancies and the release of electrons. The difference between the maximum and minimum sense resistor values can be as high as 74KΩ at a temperature of 830^0C. In addition, the calculated average response time (τ), which is defined as the time required for the sense resistor response to go from zero to 90% of its saturation value, yields a response of approximately 24.7 sec for the proposed oxygen sensor time. This short response time can be explained by a large area of interface oxygen vacancies and a large electron release rate. It has also been found experimentally that the sensing temperature is comparable to the previous published paper (Ogita et al., 2003), [4] the temperature of the deviation can be attributed to the results obtained from different measurement systems, or because the component has a large sensing structure.

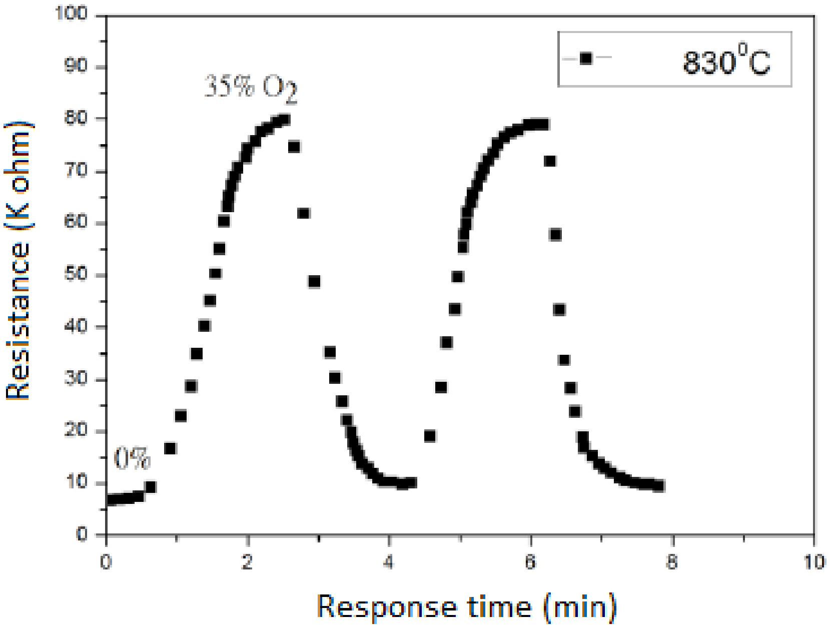


Figure 6: Dynamic change diagram of resistance under different oxygen concentration changes

In addition, the mathematical definition of oxygen sensitivity can be written as follows:

$$S(\%) = \frac{R_g - R_a}{R_a} \times 100\% \tag{5}$$

Where R_g and R_a are the sense resistor values in the atmosphere and oxygen, respectively. The effect of oxygen sensitivity on temperature change at a fixed 30% O_2 concentration is shown in Figure 7. From the experiment, it was found that the highest sensitivity is as high as 70% at a temperature of about 810°C. This phenomenon can be attributed to the surface etching type. The detector has a structure that senses a large surface area.

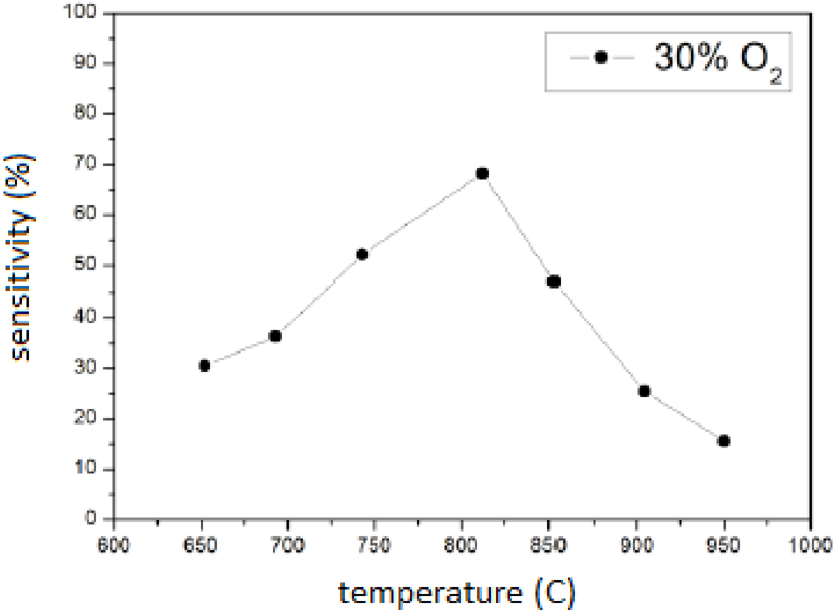


Figure 7: The relationship between temperature and sensitivity when the oxygen concentration is fixed at 30%

In addition, the experiment also tried to observe the change of the induction resistance with the continuously changing oxygen concentration, that is, when the temperature was 900°C at different times, the oxygen concentration of 15%, 25%, 40% was introduced to observe its dynamic response. The experimental results produced different and measurable fluctuating resistance values at different oxygen concentrations, and the response of the sensor was good and reproducible. From 15% oxygen concentration to 35%, the increased sensor resistance and resistance change is mainly due to the influence of electrons on electrical conduction. The experimental results show that at 40% concentration, the difference between the maximum and minimum sensed resistance values can be as high as 90KΩ. The formula can be written as a function of different temperatures.

$$R(T_2) + R(T_1) + \Delta R = R(T_1)\left[1 + \gamma(T_1) \cdot \Delta T\right] \tag{6}$$

After finishing the above formula, referring to the simple voltage dividing circuit shown in Fig. 8, the relationship between the output voltage V_o and the temperature can be obtained as follows:

$$V_o(T_1) = \frac{V_{CC}}{1 + \frac{R_2}{R_L}} \tag{7}$$

$$V_o(T_2) = \frac{V_{CC}}{1 + \frac{R_2}{R_L}\left[1 + \gamma(T_1) \cdot \Delta T\right]} \tag{8}$$

In this simple voltage divider circuit, the condition is 15% O_2, and when the DC voltages V_{CC}=5V and R_L=50KΩ are used, the output voltage is correlated with temperature, and the measurement temperature is changed from 600 to 1000°C. As shown in Fig.8, the measured V_o value is equal to 3.2V at 600°C, and the calculated corresponding value is the oxygen sensor resistance with 28kΩ. The calculation method is as follows:

$$3.2=5 \times [50/(R2+50)] \tag{9}$$

Calculated by the above formula, R_2 = 28 (kΩ). Further, it is understood from Fig. 8 that the output voltage tends to be saturated at a temperature close to 1000°C, and V_o = 2V is measured at this temperature, which corresponds to an oxygen sensor resistance of 75 kΩ. Testing the voltage output from a simple voltage divider circuit can also reconfirm that an increase in temperature will result in an increase in the resistance of the oxygen sensor of the gallium oxide.

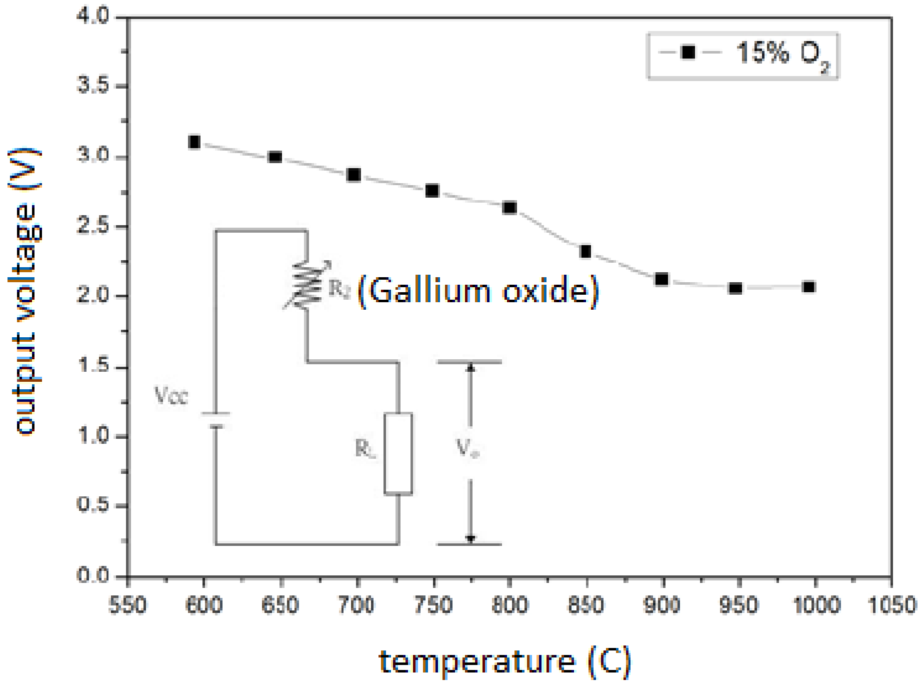


Figure 8: The relationship between output voltage and temperature under voltage divider circuit test; illustration is oxygen sensor divider circuit test

The oxygen sensing characteristics of gallium oxide can be tested by a simple voltage dividing circuit as shown in the inset of Fig. 8. For an oxide semiconductor, the coefficient of thermal expansion can be expressed by the following formula:

$$\gamma(T) = \frac{1}{R}\frac{dR}{dT} \tag{10}$$

Where γ is the air excess ratio. Under temperature changes, the equation for resistance change can be rewritten as follows:

$$\Delta R = \gamma(T) \cdot R \cdot \Delta T \tag{11}$$

Since the oxygen sensor resistance varies with temperature and oxygen concentration, the most popular and accurate method of detecting resistance changes is by using a Wheatstone bridge, as shown in the inset of Figure 9. If V_{cc}, R_1, R_3, and R_4 are set to 5V, 100KΩ, 50KΩ, and 100KΩ, respectively. The internal voltage difference, Vo is derived using the circuit formula will be equal to:

$$V_o = V_+ - V_- = V_{CC} \cdot \left(\frac{R_4}{R_1 + R_4} - \frac{R_3}{R_3 + R_2} \right) \tag{12}$$

At a temperature of 880°C and 15% O_2, the output voltage V_o is approximately equal to zero. The exposed gallium oxide oxygen sensor is equal to 50KΩ by the bridge balance and is measured by the Wheatstone bridge circuit. The output voltage is the same as the oxygen concentration. The dependency is shown in Figure 9. When the oxygen concentration is 10%, the measured output voltage

V_o=-0.3V, the corresponding value can be calculated by formula (12) with 39KΩ; similarly, at the oxygen concentration of 35% O_2, the measured output voltage V_o=0.8V has a corresponding value of 97KΩ. Therefore, it can be seen that an increase in concentration will also result in the same result as discussed in the theoretical analysis, which would also increase the sense resistance.

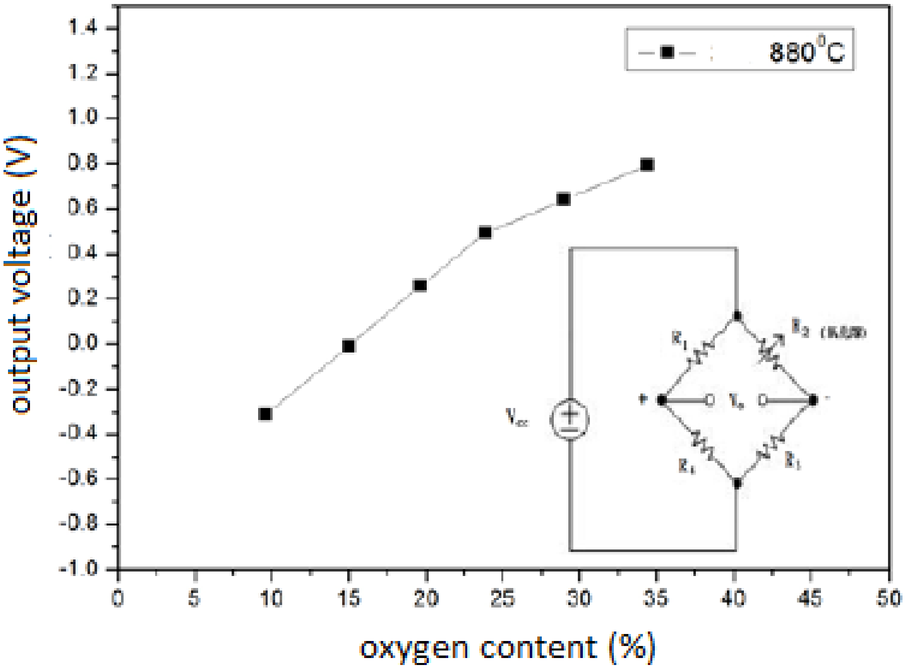


Figure 9: The relationship between the oxygen content and the output voltage at a temperature of 880°C; the illustration is the Wheatstone bridge test circuit.

VI. CONCLUSION

This thesis has successfully studied the high-temperature sensing characteristics of gallium oxide thin films. Oxygen sensors with V-groove gallium oxide surface structure with large surface area have been successfully manufactured, and a series of tests and research have been carried out at the same time. Under the use of a good quality gallium oxide film layer, the DC turn-on voltage and oxygen detection sensitivity are significantly adjustable, and its electrical characteristics are a function of oxygen concentration and temperature. A short rise time response of 24.7 sec was observed experimentally when the oxygen content changed from 0% to 35%. It can also be found from the experiment that the proposed structure has good electrical properties and high oxygen sensitivity over a wide temperature range. This new oxygen sensor also has low oxygen concentration detection sensitivity. This gallium oxide film is highly sensitive to oxygen from low to high concentrations of oxygen. In addition, using the oxygen sensing thin film resistor in the circuit design, the relative output voltage at different oxygen contents can be obtained, that is, the voltage of the conversion circuit can derive the ambient oxygen content. Therefore, this new research structure shows high sensitivity and fast response, so this component should have high potential in sensor circuit applications.

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