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DEPOSITION OF Ga_2O_3 THIN FILM FOR HIGH-TEMPERATURE OXYGEN SENSING APPLICATIONS

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Novel oxygen gas sensor based on gallium oxide thin film operated at high temperature from 700^0C to 1100^0C has been analyzed. Gallium oxide thin films have been deposited by sputtering method using a power target and their sensing properties, electrical sensitivity and response time have also been studied. Grain sizes of the material are dependent on different sputtering conditions and investigated by AFM. Two kinds of circuit operation are designed for the use of oxygen detection. The first mode could sense for the presence of 20% O_2 under different temperatures and obtain the detection of significant output levels due to the change of O_2 resistance. In the second mode of operation, a Wheatstone bridge circuit is used to get the O_2 voltage-concentration transfer plot. Based on the investigation of sensor circuit design, it would enhance our physical understanding of this kind of oxygen sensing transducer in general.

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1. Introduction

Recently, there have been increasing demands for oxygen sensing applications at high temperature which enable us to detect oxygen in exhaust system gas produced during the operation of combustion furnaces and various combustion processes. [1] A series of researches have been made for developing oxygen sensors that work at high temperature. Some oxide-based materials with standard working temperature are reported and shown in Table 1. The relation between the conductance and the oxygen partial pressure is given as [2-3]

$$\sigma = C\exp(-E_A / KT)P_{O_2}^{\frac{1}{m}} \tag{1}$$

where σ is the conductivity, C is a constant, E_A is the activation energy, K is Boltzmann's constant and P_{O2} is the oxygen partial pressure. The constant m depends on the defects involved in the conduction mechanism. From these oxygen sensors based on Ga_2O_3 is still in an advanced phase of development, it can operate at high temperature up to 1000^0C for detecting the exhausted gas by car engineers and during metallurgical processes. [4].

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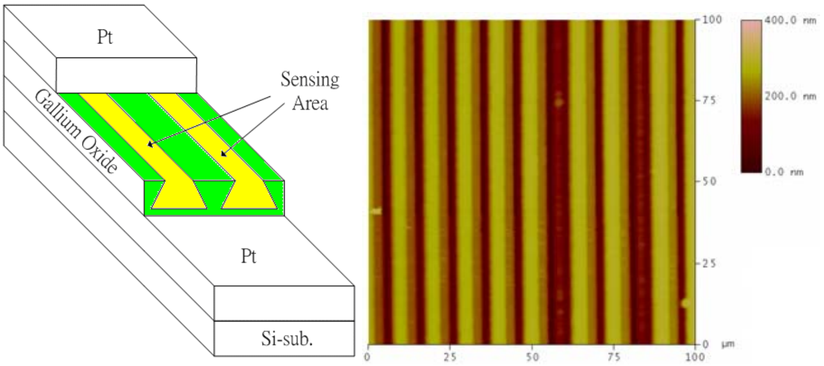
Table 1 Common oxide-based oxygen sensors and its working temperature

	working temperature (K)
TiO_2	973-1073
CeO_2	973-1373
SnO_2	573-773
ZnO	573-773
Nb_2O_5	673
Ga_2O_3	1173-1273

In this study, Ga_2O_3 thin films are prepared by the sputtering growth technology. For the film quality, it is very important to control the sputtering condition for the decrease of the drain sizes and improvement of the response characteristics. A Ga_2O_3- etched sandwich structure with Pt electrodes is used to investigate the oxygen sensing ability. A series of electrical measurements are made on the possible applications of these films on an oxygen sensor operating stably at a high temperature from 700^0C to 1100^0C.

2. Experimental

In this study, gallium oxide thin films with 1um thickness are deposited by using an RF sputtering system at 200W power, substrate temperature 950^0C and a powder target of 99.999% gallium oxide film source is employed. The Pt-Ga_2O_3-Pt sandwich structure shown in Fig.1(a) is grown on the Si substrate and the internal gallium oxide is etched with etching solution to increase the sensing area. From AFM measurement shown in Fig.1(b), it is found that the average oxide etching width is about 5um and the maximum etching depth is 0.4um. The top and bottom Pt metals are formed by the lift-off method and covered with gallium oxide thin film to make a sandwich structure for electrode protection against oxidation and its stable contact. [5] Figure 2 shows the schematic setup of the Pt-Ga_2O_3-Pt oxygen measurement. For oxygen sensing measurement, the testing devices are placed in a closed stainless-steel reaction chamber with a gas flow tube and a regulating valve to control the oxygen and nitrogen mixture gas. The device output is connected to the semiconductor parameter analyzer. During the experiment, different concentrations of oxygen gas are employed in this study. The chamber is maintained at one atmosphere pressure with a continuous and stable gas flow rate.



(a) (b)

Fig.1 (a) Schematic cross-section of the Pt-Ga_2O_3-Pt oxygen sensor (b) AFM image of the etched Ga_2O_3 thin film.

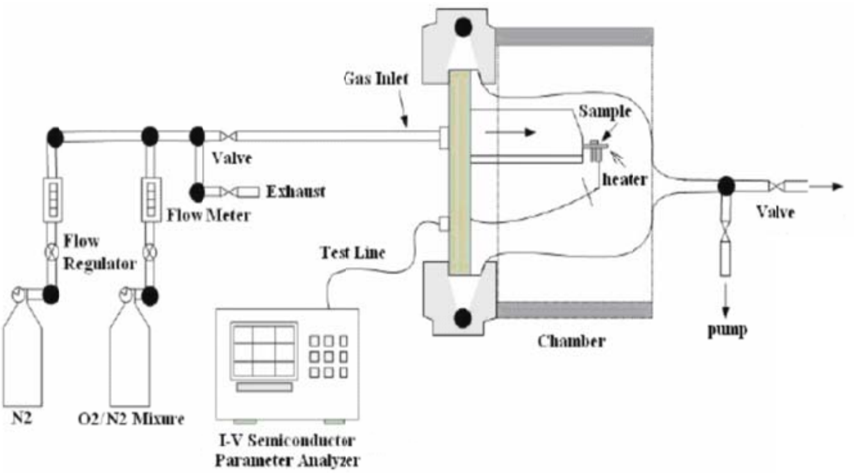


Fig.2 Schematic setup of the oxygen measurement system

3. Results and discussion

Oxygen sensing mechanism can be explained as follows: metal oxide adsorbs oxygen molecules at high temperatures and converts them into ionized molecules of O_2^- or ionized atoms, i.e. O^- or O_2^- which leads to electrons being extracted from the conduction band. [6] And then, the surface states are modified by reducing the carriers and forming a depletion region near the semiconductor interface. While oxidizing gases occupied the sensor surface, more oxygen will be adsorbed at the surface and then would attract more electrons from conduction band. This kind of reaction results in the decrease of surface conductivity and can be written with the following equations given as:

$$O_2(gas) \Leftrightarrow O_2(ads) \tag{2}$$

$$e^- + O_2(ads) \Leftrightarrow O_2^-(ads) \tag{3}$$

$$e^- + \frac{1}{2}O_2 \Leftrightarrow O^-(ads) \tag{4}$$

Thus, an amorphous Ga_2O_3 thin film may be utilized as a good gas sensor with oxygen deficiency. [7] The improved electrical conductivity can be considered that the existence of many unoccupied bonds which are induced by oxygen vacancy. Based on the physical understanding of the principle of oxygen sensor, the etched Ga_2O_3 sandwich structure is proposed and may exist much more unoccupied bonds and high sensitivity to oxygen gas can be expected in this study.

In Fig.3, the AFM images show the different grain surface of Ga_2O_3 thin film deposited from a powder target at the sputtering pressures, i.e. 5Pa, 4Pa, 3Pa, 2Pa, respectively. It is found that the grain surface of the deposited thin film at a low sputtering pressure has larger grain sizes than that made at a high sputtering pressure. Thus, the observed average grain size of the deposited thin film is getting larger from Fig.3(a) to (d). From experiment, the deposited thin film after heat annealing also increases the grain size while increasing the substrate temperature. After film growth, the Ga_2O_3 oxygen sensing property is checked by a simple electrical partial-voltage circuit which is shown in Fig.4(a). For an oxide semiconductor, the thermal coefficient is given by the equation:

$$\gamma(T) = \frac{1}{R}\frac{dR}{dT} \tag{5}$$

where the γ is the air excess ratio [8-10], R is the resistance and T is absolute temperature, respectively. If the temperature is changed from T_1 to T_2, the change of resistance in Eq.(5)

will be given as:

$$\Delta R = \gamma(T) \cdot R \cdot \Delta T \tag{6}$$

In addition, the temperature dependence of resistance R(T) can be expressed as:

$$R(T_2) = R(T_1) + \Delta R = R(T_1)[1 + \gamma(T_1) \cdot \Delta T] \tag{7}$$

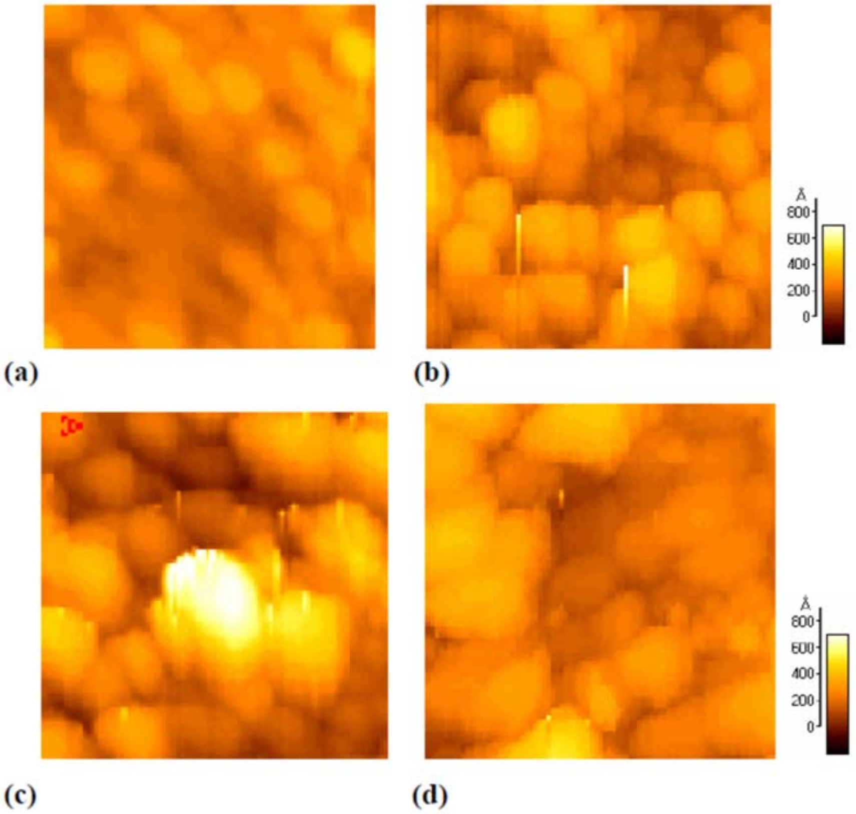
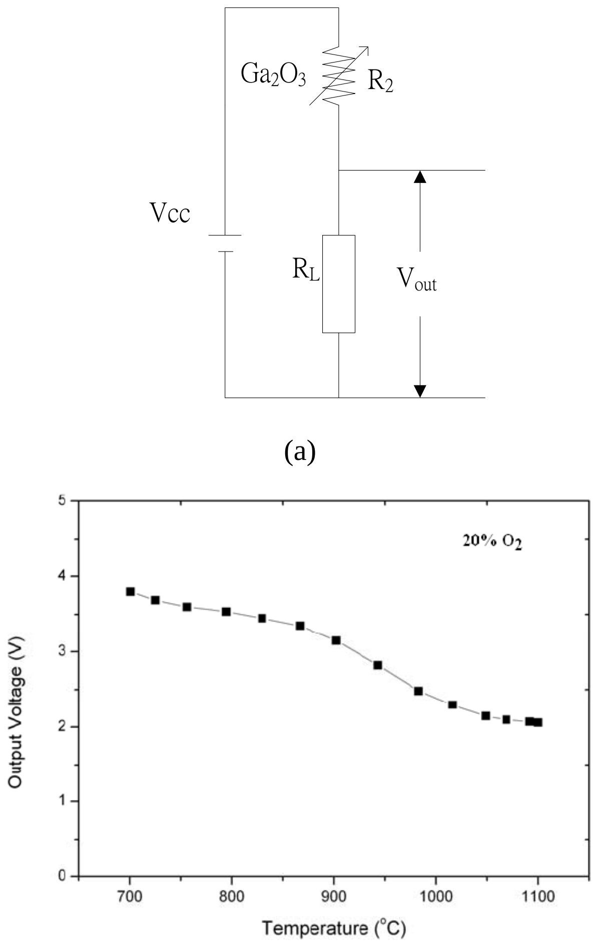


Fig.3 AFM image of Ga_2O_3 thin films deposited by RF sputtering at the sputtering pressures (a) 5Pa (b) 4Pa (c) 3Pa (d) 2Pa. The total width in the individual figure is 2um.

According the equations above and Fig.4(a), the output voltage corresponding to temperature are

$$V_{out}(T_1) = \frac{V_{CC}}{1 + \frac{R_2}{R_L}} \tag{8}$$

$$V_{out}(T_2) = \frac{V_{CC}}{1 + \frac{R_2}{R_L}[1 + \gamma(T_1) \cdot \Delta T]} \tag{9}$$



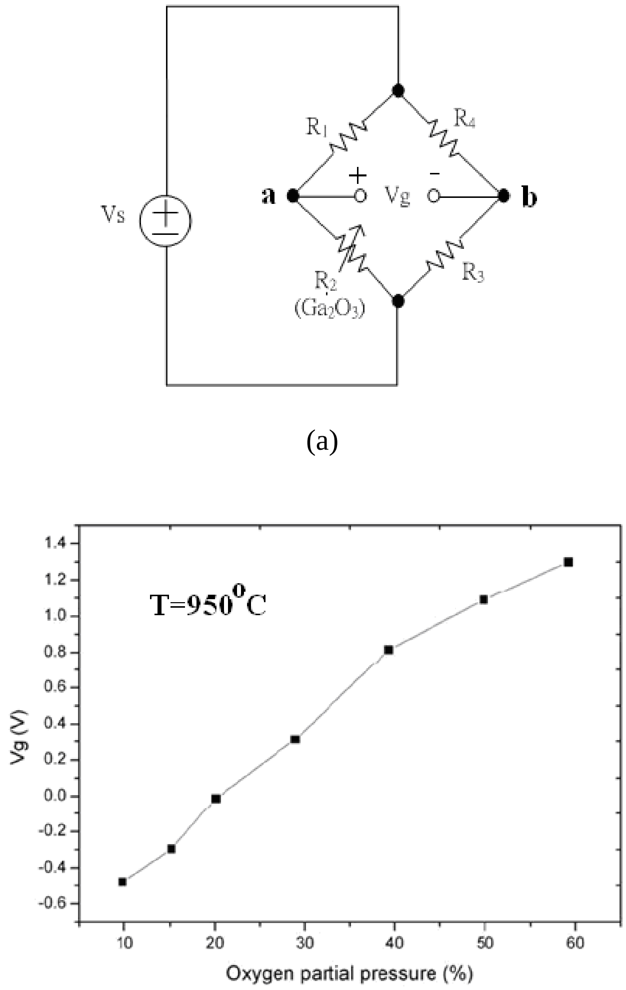
(a)

(b)

Fig.4 (a) Electrical partial-voltage circuit for measuring oxygen sensor resistance (b) Temperature dependence of the output voltage V_{out} with the oxygen sensing resistance circuit

In this circuit, the 20% O_2, DC voltage V_{CC}=5V and R_L=50KΩ are used, respectively. The temperature dependence of the output voltage is measured at temperature from 700 to 1100^0C. In Fig.4(b), the measured V_{out} at 700^0C is equal to 3.6V which is corresponding to 20KΩ for the oxygen sensor. In addition, the output voltage saturates while temperature over 1000^0C, the measured V_{out} is equal to 2.1V which is corresponding 70KΩ. From the measurement of the voltage output, it can be confirmed that the increase of temperature will result in the increase of resistance for the Ga_2O_3 oxygen sensor. Since the oxygen sensor resistance changes with respect to exposed temperature and oxygen concentration, the most popular and accurate way of detecting resistance changes is through the use of Wheatstone Resistive Bridges which is shown in Fig.5(a). If the V_S, R_1, R_3, R_4 are set to 5V, 100KΩ, 50KΩ, 100KΩ, respectively. The internal voltage difference, V_g is equal to:

$$V_g = V_a - V_b = V_s \cdot \left(\frac{R_2}{R_1 + R_2} - \frac{R_3}{R_3 + R_4}\right) \tag{10}$$



(a)

(b)

Fig.5 (a) Schematic Wheatstone Resistive Bridge circuit for measuring oxygen sensor resistance (b) Oxygen dependence of the output voltage V_g with the oxygen sensing resistance circuit

At temperature of 950^0C and with 20% O_2, the exposed Ga_2O_3 oxygen sensor is similar in resistance with 50 KΩ, and the output voltage, V_g is approximately equal to zero. Through the Wheatstone Resistive Bridge circuit, the oxygen dependence of output voltage is measured at 950^0C and shown in Fig.5(b). When the oxygen concentration is 10%, the measured output voltage, V_g is -0.5V which is corresponding 30KΩ for the oxygen sensor. Under 60% oxygen concentration, the measured output voltage, V_g is 1.4V which is corresponding to 150KΩ. Thus, it is found that the increase of O_2 concentration will also result in the increase of sensor resistance which has the same result as discussed with theoretical analyses.

In addition, the dynamic response for different O_2 concentrations at 20%, 40% and 60% for the Ga_2O_3 oxygen sensor at 900^0C is shown in Fig.6 which indicates the ability to produce a different and measurable resistance at different O_2 concentrations. Good repeatability for the sensor response is evident from the observed measurement. The increased sensor resistance and variation in resistance while increasing oxygen concentration from 20% to 60% indicate that the electrical conduction is due to electrons. The variation sensor resistance between the maximum and minimum is up to 90KΩ at 60% O_2 concentration.

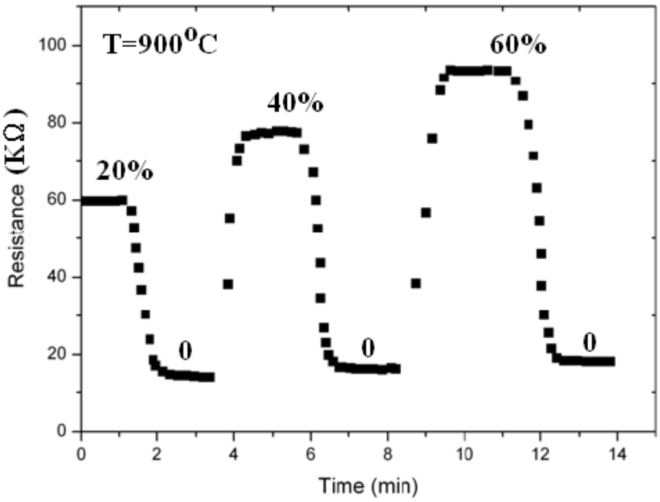


Fig.6 Dynamic response of the gallium oxide with different O_2 concentrations at 900^0C

4. Conclusion

Ga_2O_3 thin films having a thickness of 1um are deposited by the RF sputtering technique. They are electrically characterized as a function of the oxygen concentrations and temperature. The film quality is relative to the growth pressure. The sensing characteristics of the gallium oxide at high temperature have also investigated. This kind of oxide film could be useful for sensing low to high concentration of oxygen and thus suggest that it has the potential application as an oxygen gas sensor.

References

[1] P. Moseley, Sensors and Actuators B, **6-7**, 149 (1992).
[2] M. Fleischer and H. Meixner, Sensors and Actuators B, **6-7**, 257 (1992).
[3] V. Demarne, R. Sanjines, D. Rosenfeld, F. Levy and A. Grisel, Sensors and Actuators B, **6-7**, 704 (1992).
[4] C. Baban, Y. Toyoda and M. Ogita, J. Optoelectronics and Advanced Materials, **7**, 891 (2005).
[5] C. Baban, Y. Toyoda and M. Ogita, Thin Solid Films, **484**, 369 (2005).
[6] B. Wang, J. Iqbal, X. Shan, G. Huang, H. Fu, R. Yu, D. Yu, Mater. Chem. Phys., **113**, 103 (2009).
[7] H. Hanto, T. Minami, S. Takata, J. Appl. Phys., **60**, 482 (1986).
[8] Y.D. Wang, X.H. Wu and Z.L. Zhou, Sensors and Actuators B, **73**, 216 (2001).
[9] Y.D. Wang, X.H. Wu and Z.L. Zhou, Solid-State Electron., **44**, 1603 (2000).
[10] M.M. Hedges and M.J. Bannister, Key Eng. Mater., **53**, 263 (1991).