Electron transport mechanism of thermally oxidized ZnO gas sensors

N. H. Al-Hardan, M. J. Abdullah and A. Abdul Aziz
School of Physics, Universiti Sains Malaysia (USM), 11800 Minden, Pulau Pinang, Malaysia

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ZnO gas sensor was prepared by thermal oxidation of metallic Zn for different time period. The sensors were characterized by I-V measurement with dc voltage ranging from -2 to 2 volt, in both normal air and H_2 gas concentration from 40 to 160 ppm. The transport mechanism of the carriers was believed to be thermionic process through both the grain boundaries and the metal–semiconductor junctions. The resistance of the ZnO sensing film is independent of the applied voltage in the range of $0.5 < V_G < 2$ V and depends only on the gas concentration in the range of 40 to 160 ppm, which make it useful for gas sensing application.

I. INTRODUCTION

Metal-oxide devices change their resistivity in the presence of reducible or oxidation gases. They have been used since 1971 [1] when Taguchi introduced to the market its metal oxide gas sensor based on the SnO_2 ceramics. Many published works try to explain the mechanism involved in the gas detection process. Most of these works depend on measuring the change of the resistance as a function of the gas concentration (sensitivity) and type of the gas (selectivity). Essentially, the method detects the sum of different effects (grain, grain boundary and metal–semiconductor contacts) that occur in the surface of the sensor [2].

Among numerous metal oxides that have been investigated such as TiO_2, V_2O_5 [3], SnO_2 [4], WO_3 [5] and ZnO [6], SnO_2 and ZnO had received more attention because of their non toxic, good and stable electrical properties.

ZnO thin film had been extensively studied by many researchers due to its diverse applications in different modern technological fields such as gas sensors [6], conductive transparent layers for solar cell and displays application, and surface acoustic wave sensors. ZnO thin film had been prepared by different methods such as DC and RF sputtering, sol–gel and thermal pyrolysis [7] and oxidation of Zn precursor such as ZnS and Zn [8,9].

Present work investigates the electron transport mechanism of the ZnO gas sensor in the presence of different concentration of H_2 based on the thermo-emission theory. The study will focus on the current–voltage and resistance –voltage characteristics of the gas sensor in the voltage range from -2 to 2 volt.

II. MATERIAL AND METHODS

Thin film ZnO gas sensors were fabricated on n-type Si (1 0 0) wafer, which had been initially cleaned by RCA standard method and oxidized to form an insulating layer of SiO_2. Photolithography was employed to pattern the Ti/Pt heat element and the conducting electrodes. Ti and Pt was coated using Edwards A306 dc magnetron sputtering unit, followed by wet etching process to get the final device. Thin films of Zn metal (dimension: 2 mm × 2 mm) with good uniformity were coated using high purity (99.99%) Zn target. The ultimate pressure of the unit was 1×10^{-5} Torr and was raised to 4×10^{-3} Torr during the process by flowing high purity Ar (99.999%). Thermal oxidation of the Zn films was carried out in a horizontal controlled tube furnace by introducing the samples into the furnace at room temperature. The temperature was then raised at the rate of 5^o C.min^{-1} to 400^o C in high purity O_2 (99.99%) atmosphere for 30 and 60 minutes. The thickness of the ZnO films was measured by optical method using Filmmteric Model 20, which was about 0.3 micron. Fig. 1 shows the schematic layout and cross section of the device structure.

The I-V characteristic of the produced device was measured using a programmable Electrometer – model 617 KEITHLEY, which also supplied the voltage V_G in the range from -2 to 2 volt. DC power supply type Lodestar (30V/3A) was used to supply the current to the heating elements. A calibrated Chromel-Alumel thermocouple was mounted on the device to measure the operating temperature of the sensor, which was maintained at 400^oC. The measurements were commenced after 3 minutes of turning on the gas flow.

All the measurements were taken at room temperature with humidity of 62%. The test chamber was made of stainless steel with glass cover at the top part, creating volume of about 8200 cc. The gas concentration was controlled by changing the flow rate of the gas and was in the range from 40 to 160 ppm.

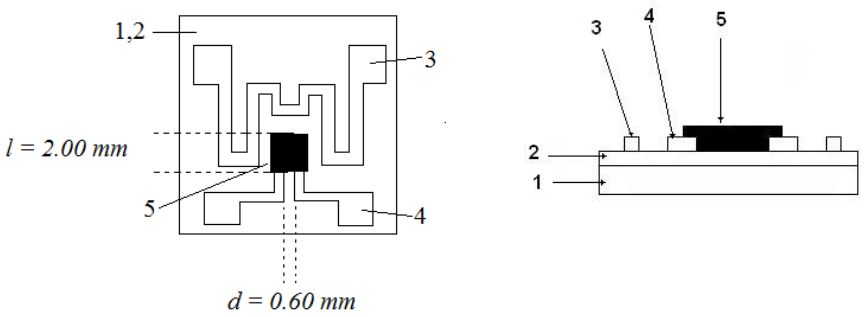

FIG. 1. The schematic cross section and top view of the prepared gas sensor; 1- Si substrate, 2- SiO_2 layer, 3- Ti/Pt heating element, 4- Ti/Pt electrodes and 5- ZnO thin film.

III. RESULTS AND DISCUSSION

Current–voltage characteristic of ZnO thin film prepared by thermal oxidation of Zn metal for 30 and 60 minutes are shown in Fig. 2. Results of XRD (not shown) proved the complete conversion of the Zn metal to polycrystalline ZnO. The surface morphology of the film exhibits columnar grain growth which is important for gas sensing applications [10]. It is obvious that the forward current is enhanced with the H_2 concentration but better resolution of the measured current was obtained for the 30 minutes sample. This may be due to the presence of the more numbers of oxygen vacancies acting as donor within the ZnO band gap. For samples with longer oxidation time, the number of the oxygen vacancies will be less [11].

The increase in applied voltage results in the lowering of the barrier height at the metal–semiconductor interface, thus enhances the output current. In addition, the increase of H_2 concentration would cause a reduction in the barrier height between the grain boundaries and enhances the current [12] as more electrons are released.

The chemical reaction that causes the release of electrons at the surface of the metal oxide gas sensors for reduction gases such as H_2 at elevated temperatures (300^o–400^oC), is given by [13];

$$H_2 + O^- \rightarrow H_2O + e^- \quad (1)$$

where O^- is the chemisorptions species on the surface of ZnO at elevated temperatures.

The electron transport mechanism can be modeled based on the work by Stephanie *et al*. [5], who showed that the mechanism depends on the carrier concentration of the semiconductor. For low carrier concentration the width of the potential barrier is large and only the electrons of sufficient kinetic energy able to move over the barrier. At high carrier concentration, the electrons will have the ability to tunnel through the narrow potential barrier. The first mechanism is known as thermionic emission which is dominant for the Schottky contacts, while the second one is ascribed to electron tunneling [13].

The theoretical R-V (Resistance–Voltage) characteristic associated with thermionic emission and electron tunneling mechanism is shown in Fig. 3 [5].

Fig. 4 shows the R-V characteristic obtained for the ZnO gas sensor. It can be inferred that the electron transport in the gas sensor is associated with the thermionic process. At low applied voltage of $-0.5 < V < 0.5$ volt, the resistance of the film is non constant for the both samples, which means that the I-V curves are not linear. For voltage $0.5 < V < 2$, $-2 < V < -0.5$ volts, the resistances of both samples are almost constant (independent on voltage). In this region, the H_2 concentration affects the resistance of the sensing element; the higher the concentration the lower is the resistance. This dependence is very useful in gas sensing application and widely used for the determination of gas concentration in atmosphere.

The linear dependence of the resistance on gas concentration for the samples with 30 minutes thermal oxidation is better than that the of 60 minutes samples, which can be applied for sensing the H_2 concentration in the studied range. For samples with 60 minutes oxidation, good resistance resolution only appears in the concentration range of less than 80 ppm. The near saturation in the resistance magnitudes (above 80 ppm) for this sample suggests that the donor concentration begins to be limited [14].

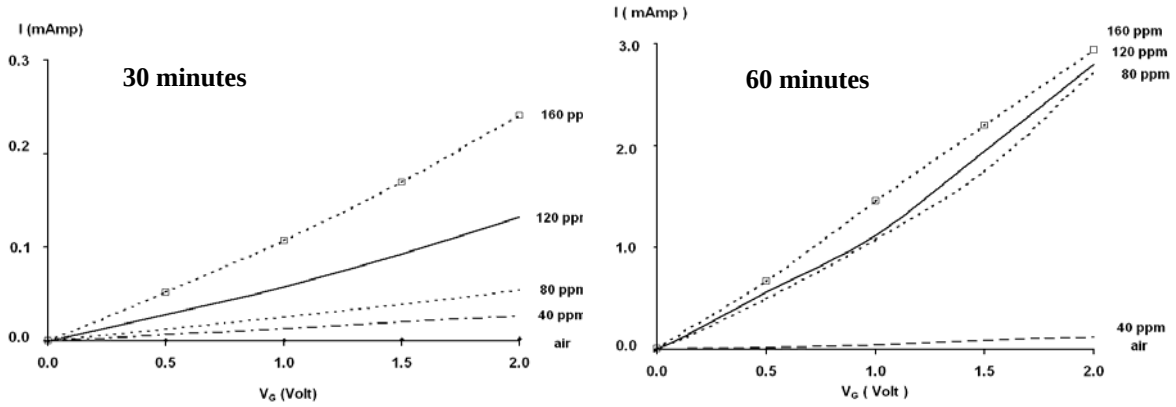

FIG. 2. The forward current–voltage characteristic of ZnO gas sensor oxidized at 30 minutes and 60 minutes for different H_2 concentration. The operating temperature is 400°C.

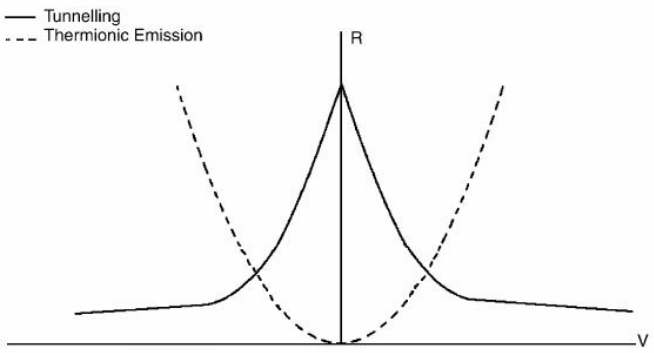

FIG. 3. Theoretical R-V characteristics associated with thermionic emission and tunneling [5].

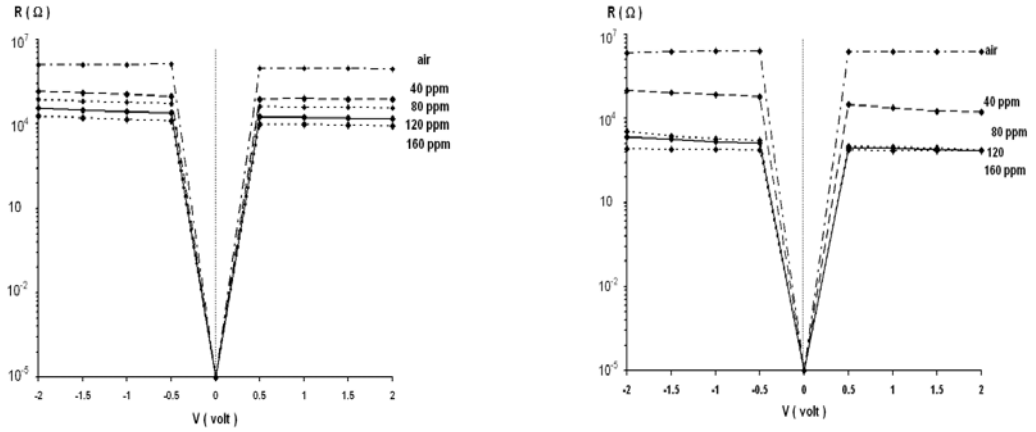

FIG. 4. The R-V characteristic of the ZnO gas sensor for (a) 30 minutes and (b) 60 minutes samples.

IV. CONCLUSION

The electron transport of ZnO gas sensor prepared by thermal oxidation of Zn metal is attributed to the thermionic emission mechanism. The resistance of the sensor decreased with the H_2 concentration in the range from 40 to 160 ppm. The sensors prepared for 30 minutes show better sensing characteristics as compared to that of the sensors prepared for 60 minutes.

ACKNOWLEDGEMENTS

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REFERENCES

[1] N. Taguchi, US Patent 3,625,756 (1971).
[2] P. T. Mosely and B. C. Tofield, *Solid State Gas Sensor*, Adam Hilger, Bristol and Philadelphia (1987).
[3] Hayakawa, Y. Iwamoto, K. Kikuta and S. Hirano, Sensors and Actuators B, **62**, 55 (2000).
[4] O. Schilling and K. Colbow, Sensors and Actuators B, **21**, 151 (1994).
[5] K. H. Cha, H. C. Park and K. H. Kim, Sensors and Actuators B, **21**, 91 (1994).
[6] S. Pitcher, J. A. Thiele, H. Ren and J. F. Vetelino, Sensors and Actuators B, **93**, 454 (2003).
[7] P. P. Sahay, J. Materials Science, **40**, 4383 (2005).
[8] Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S. J. Cho and H. Morkoç, J. Appl. Phys. **98**, 041301 (2005).
[9] S. Cho, J. Ma, Y. Kim, Y. Sun, G. K. L. Wong and J. B. Ketterson, Appl. Phys. Lett., **75**, 2761 (1999).
[10] X. T. Zhang, Y. C. Liu, Z. Z. Zhi, J. Y. Zhang, Y. M. Lu, W. Xu, D. Z. Shen, G. Z. Zhong, X. W. Fan and X. G. Kong, J. Cryst. Growth, **240**, 463 (2002).
[11] Z. Dachun, Q. Zhongkai, P. Xiaoren, D. Muji and S. Minggen, J. Vac. Sci. Technol. B, **15**, 805 (1997).
[12] J. L. Baptista and P. Q. Mantas, Journal of Electroceramics, **4**, 215 (2000).
[13] N. Barsan and U. Weimar, Journal of Electroceramics, **7**, 143 (2001).
[14] S. Kim, B. S. Kang, F. Ren, K. Ip, Y. W. Heo, D. P. Norton and S. Pearton, J. Appl. Phys. Lett., **84**, 1698 (2004).