Enhancement of gas response of annealed ZnO film for hydrogen gas detection

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Abstract

The mechanism of hydrogen (H_2) gas sensor in the range of 50-200 ppm of RF-sputtered annealed zinc oxide (ZnO) and without annealing was studied. The X-ray Diffraction(XRD) results showed that the Zn metal was completely converted to ZnO with a polycrystalline structure. The I–V characteristics of the device (PT/ZnO/Pt) measured at room temperature before and after annealing at 450 ^oC for4h, from which a linear relationship has been observed. The sensors had a maximum response to H_2 at 350 ^oC for annealing ZnO and showed stable behavior for detecting H_2 gases in the range of 50 to 200 ppm. The annealed film exhibited higher response than the film without annealing.. The sensing mechanism was modeled according to the oxygen–vacancy model.

Key words

RF-sputtering , Zinc oxide, Gas sensor, Oxygen-vacancy model.

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تعزيز استجابة غشاء اوكسيد الخارصين الملدن للكشف عن غاز الهيدروجين

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الخلاصة

درست في هذا البحث ميكانيكية تحسس متحسسات الهيدرجين من تركيز 50 الى 200 جزء بالمليون لاغشية ZnO الملدنة بدرجة 450 درجة مئوية لمدة اربعة ساعات وللاغشية غير الملدنة والمحضرات بطريقة RF-sputtering. واظهرت نتائج فحوصات الاشعة السينية تكون غشاء اوكسيد الخارصين متعدد التبلور، وكما اظهرت قياسات تيار – فولتية للمتحسس بلاتين/اوكسيد الخارصين/بلاتين قبل التلدين وبعده وجود علاقة خطية للغشاء الملدن. واظهرت نتائج استجابة الغشاء الملدن كانت اقصاها في درجة حرارة 350 درجة مئوية. كما واظهرت النتائج ان سلوك مستقر في استجابة المتحسسات لتراكيز الهيدروجين من50-200 جزء بالمليون واستجابة اعلى للاغشية الملدنة. واعتمد على نموذج اوكسجين- فراغ في تفسير ميكانيكية التحسس.

Introduction

Metal oxide semiconductors (MOS) are well known as multifunction materials and gas sensing application employing MOS is one of the most studied areas [1,2]. The sensing mechanism depends on the change of the resistance of the MOS in the presence of the gas under test, in which the gas adsorption led to a charge transfer between the chemisorption oxygen and the MOS surface. The oxygen molecules from the ambient atmosphere are initially adsorbed at the MOS surface follows by the extraction of electron from the conduction band of the MOS material. The oxygen molecule is then converted to a single or a double oxygen ion and become ionosorbed on the surface. This leads to a decrease in electron concentration in the material and consequently, the increase in resistance. The reaction of these gases such as hydrocarbons or any reduction

gases with the ionosorbed (O_ads) will result in the release of the captured electrons back to the conduction band thereby increasing the electron concentrations, which in turn decreasing the resistance [2]. Nanostructure ZnO is a promising material for chemical gas sensors because of its large surface-to-volume ratio, which improve its response [3,4]. ZnO gas sensors were recently studied extensively due to the simplicity of its preparation, high chemical stability and it has been prepared by different methods, such as radio frequency (RF) sputtering [5], sole-gel [6], and oxidation of Zn metal [7].

Hydrogen becomes one of the resources of clean energy, since the burning of the H_2 is water, which is decomposed again into hydrogen and oxygen. It has a wide range of flammability in air, which is about 4–75% by volume and the lowest limit of H_2 concentration in air to cause explosion is 4.65% [8,9]. This makes it more flammable than other fuels. Therefore there is a need for a device which is capable of detecting low levels of H_2 [10]. Semiconductive metal-oxide (MO_x) sensors were studied and used extensively for hydrogen detections for their simplicity, reliable, low-cost and easily mass produced [11], and among them were tungsten oxide (WO_3) [12], tin oxide (SnO_2) [13] and zinc oxide (ZnO) [14]. Nanostructured ZnO is a promising material for chemical gas sensors due to its large surface-to volume ratio [14,15]. For enhancement H_2 gas response is used the annealed ZnO film prepared by RF reactive co- sputtering technique to lead high response.

The conductance of the prepared ZnO can be expressed as [16,17]

$$G = n_o e\mu \frac{W}{L} \qquad (1)$$

where n_o is the surface carrier concentration, e is the electronic charge, μ is the mobility of the electrons, W and L are the width and length of films. On reaction of the target gas with the ZnO surface, the conductance of ZnO film will change as a result of the change in the carrier concentration Δn_s. Thus the change in conductance can be written as

$$\Delta G = \Delta n_s e\mu \frac{W}{L} \qquad (2)$$

Hence, a measure of the gas sensitivity is given by the following [16,18]

$$\frac{\Delta G}{G} = \frac{\Delta n_s}{n_o} \qquad (3)$$

The gas sensors were exposed to a fixed concentration of H_2 (100 ppm), and the temperature was varied between 200 and 450 ^oC with 50 ^oC increments at a rate of 3 ^oC per min. The sensor temperature was controlled by adjusting the applied voltage to the heating element. The measurement began 3 min after introducing gas into the test chamber. By taking the sensitivity (S) of the sample as given by

$$S(\%) = \frac{\Delta R}{R_a} \; x100 \qquad (4)$$

or response

$$s = \frac{R_a}{R_g} \qquad (5)$$

where R_g and R_a represent the resistance of the sensor in the gas and air atmosphere, respectively, ΔR refer to the difference of these resistance ($\Delta R = R_g - R_a$), the samples' response was evaluated at different operating temperatures.

Experiment

Suitable electrodes and heating element were patterned after the deposition of platinum metal (Pt). The sputtering A500 Edwards RF magnetron unit was used to prepare ZnO with a thickness of 0.25 μm and area of 2 x10 mm^2 by reactive sputtering with a power of 230 W at room temperature through Pt electrodes. The base pressure was $1x10^{-6}$ mbar, which was raised to 2.3 $x10^{-2}$ mbar by purging the chamber with high-purity argon and 80% oxygen gases, through

separate gas flow controllers. The high-purity Zn metal target was initially exposed to continuance plasma to clean the surface prior to the coating process. The thickness of the produced ZnO films was 0.3 μm, as measured by an optical method using the Filmetrics F20 unit thickness 15nm-70 micron wavelength 380-1050 micron. The ZnO films were characterized using Bruker D8 Advance Economical X-ray diffraction for phase identification. The current–voltage (I–V) characteristics of the Pt/ZnO/Pt device structure were measured with the DC voltage sweep from -5 V to 5 V at 50 mV increment employing the Keithley 2361 trigger controller. The sensor element was packaged with a stainless steel holder (Synkera Technologies, Inc.) shown in Fig.1(a). The sensor temperature was controlled by modulating the power of the micro-heater underneath the alumina substrate. The temperature of the gas sensor at various heater powers was measured using an IR temperature sensor (Rayomatic 14814-2, Euroton IRtec Co., Ltd.) Fig. 1(b). The temperature of the sensor surface (denoted as 'coated') was 20–40 °C lower than that of the bare alumina substrate (denoted as 'uncoated'). Accordingly, the sensor temperature was defined as the average between the surface temperature of the sensing layer and the bare alumina substrate.

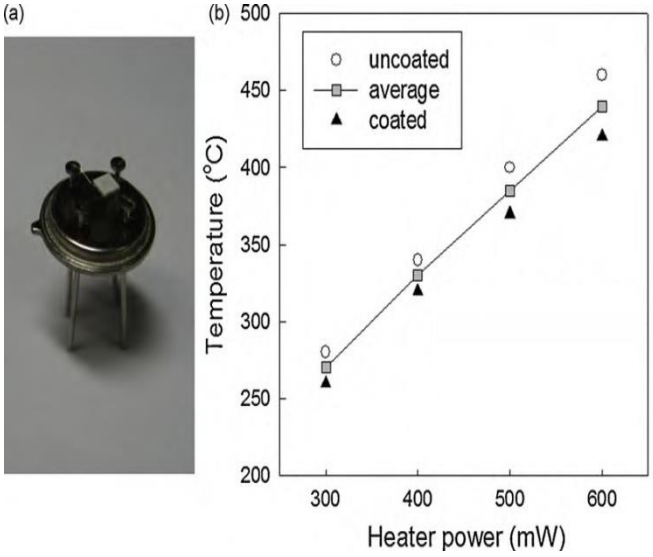

Fig.1(a): Sensor structures, (b) sensor temperatures as a function of heater power.

Results and Discussion

The X-ray diffraction (XRD) of the ZnO films are shown in Fig. 2 The films were polycrystalline and there was no evidence of Zn metal in ZnO films, which confirmed the complete conversion of Zn metal to ZnO. The peaks that appeared at 2θ of 31.9°, 34.5°, 36.36°, and 47.72° represent the (1 0 0), (0 0 2), (1 0 1) and (1 1 0) respectively phases of ZnO (JCPDF card no. 36–1451). These are in good agreement with those published by Alivov et al [19].

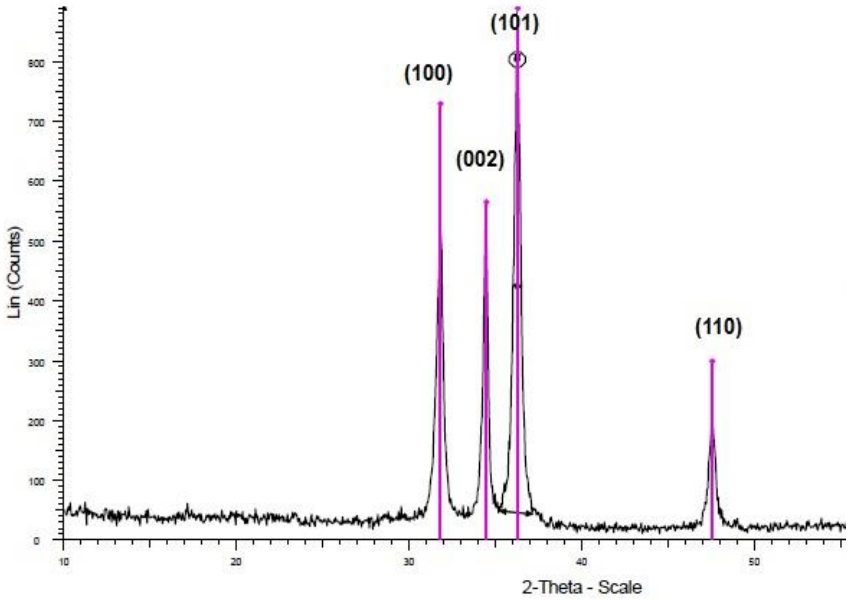

Fig. 2: XRD pattern of ZnO film.

The sensor elements are showed in Fig. 3 which shows the ZnO thin films and the Pt electrodes on Alumina substrate. The prepared ZnO thin films were observed to be highly transparent, with thickness of about (300 ± 20) nm.

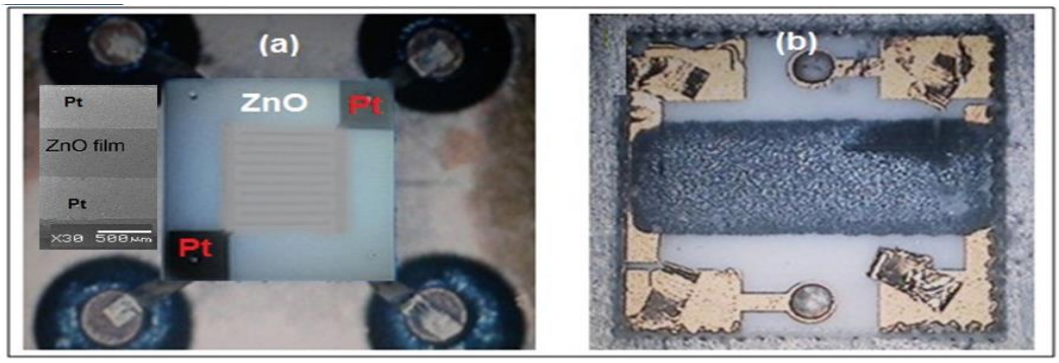

Fig.3: Sensing elements dimension of 4 mm x4 mm (a)Pt/ZnO/Pt (b)micro heater underneath.

Fig. 4 depicts the I–V characteristics of the device measured at room temperature before and after annealing at 450 ^{o}C for4h, from which a linear relationship has been observed. Such behaviour indicates the Ohmic nature of the Pt contacts which might be the consequence of high carrier concentration of the prepared ZnO, where the tunneling barrier becomes small and a quasi-ohmic contact may be created [17, 20].

The annealing process effected is obvious whereby the current of the annealed device has been enhanced indicating a decrease in the resistance of the annealed ZnO. The decrease is a result of the enhancement in the grain size of the ZnO that caused the reduction in the grain boundaries, which subsequently improved the crystal lattice deficiencies of the film.

Fig. 5 shows the dependence of the sensors response on operating temperatures (H_2

concentration was fixed at 100 ppm), which exhibits maximum response at an operating temperature of 350 ^{o}C for annealing film and

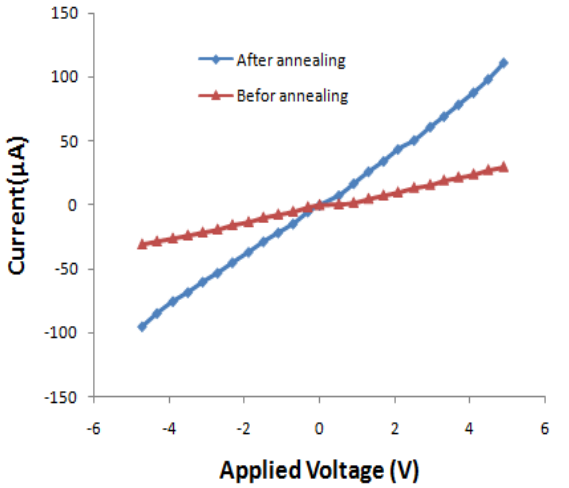

Fig.4: The I-V characteristic of the Pt/ZnO/Pt before and after annealing at 450 ^{o}C for 4h.

400 ^{o}C for a film as received (without annealing). It can be observed that the annealing ZnO sensor showed higher sensitivity at lower operating temperatures. The enhanced sensitivity at lower operating temperature is attributed to the annealing processing which led to a reduction of the grain size (grain boundaries) and an increase of the surface area.

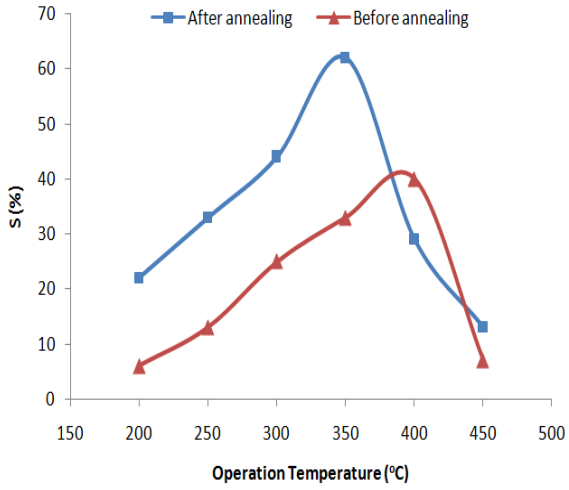

Fig. 5: The sensor sensitivity as a function of operation temperature (H_2 concentration was fixed at 100 ppm).

The sensor performance was examined in a controlled atmosphere at 350^{o}C. Fig. 6 shows the conductance changes of the Pt/ZnO/Pt sensor after annealing (450 ^{o}C for 4 h) when exposed to 100, 150, 200, 50 ppm H_2, which exhibit a measurable increasing in conductance of the sensor when exposed to H_2 gas.

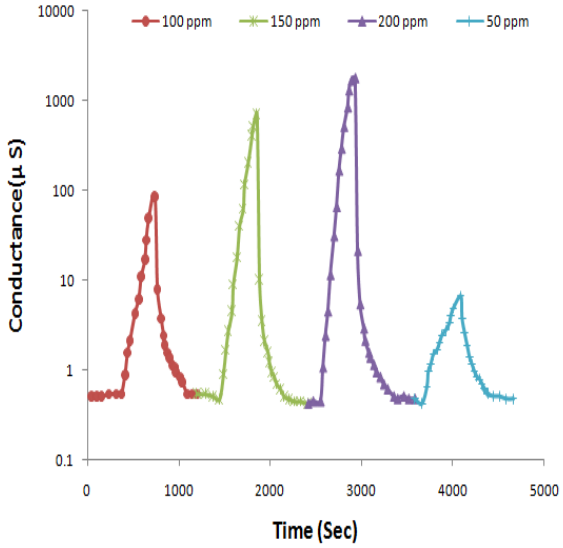

Fig.6: The conductance of ZnO gas sensor (annealed at 450 ^{o}C for 4h)under different concentration of H_2 gas at operation temperature 350 ^{o}C .

Fig. 7 shows the response of both sensors (annealed and as received) at different H_2 gas concentrations, from which it is obvious that the annealed sample shows higher response than that of the sample of 30 min oxidation. The oxygen–vacancy model may be used to explain the reaction mechanisms in this case [21–24], were the oxygen vacancies acts as electron donors. The annealing process results in the decrease of the oxygen vacancies in the samples that led to the decrease of the carrier concentrations and as consequence the resistivity is increased. The reaction with hydrogen molecules can be presents as follow, the hydrogen first reacts with the oxygen from the ZnO surface and as a consequence water vapor molecules and oxygen vacancies are

produced and electrons are introduced into the conduction band that decrease the resistance of the sensor, by purging the test chamber with air the oxygen will fill the vacancies were one or more electrons from the conduction band are captured and therefore the resistance of the sensor will increased. The reactions above can be demonstrated in the following steps [22];

$$H_2 + O_0^x \leftrightarrow H_2(gas) + V_o^x$$

$$V_o^x \leftrightarrow V_o^+ + e^-(CB)$$

$$V_o^+ \leftrightarrow V_o^{++} + e^-$$

where O_0^x is the neutral oxygen from the surface, V_0 the oxygen vacancy, V_o^x neutral oxygen vacancy, V_o^+ singly ionized oxygen vacancy, V_o^{++} doubly ionized oxygen vacancy and e^- (CB)is the electrons from the conduction band. The higher oxygen concentrations (lower oxygen vacancies) following ZnO annealed allow more reaction with hydrogen gas, thereby resulting in enhancement of the response of the sensor.

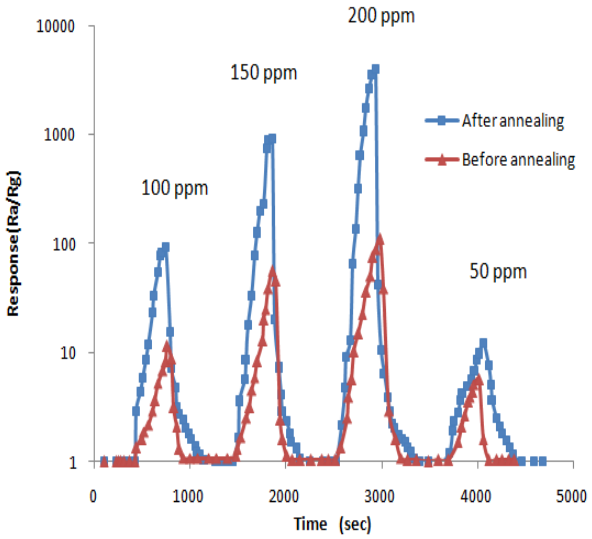

Fig.7: The response of ZnO gas sensors (annealed and as received) to different H_2 gas concentration at operation temperature (350 °C for annealed and 400 °C).

The response of both sensors at different concentrations of H_2gas is replotted as in Fig. 8. A linear relationship between the response and hydrogen gas concentration can be seen for the range up to 150 ppm for annealed ZnO gas sensor.

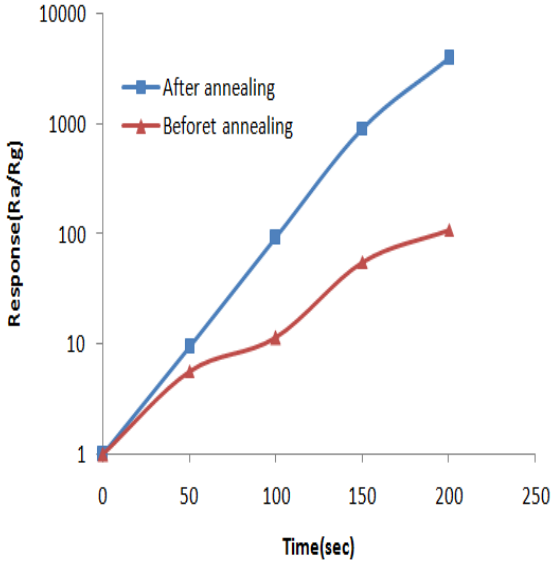

Fig.8: The response of the ZnO gas sensors((annealed and as received) as a function of H_2 gas concentration at operation temperature.

Conclusions

ZnO gas sensors were successfully prepared by RF reactive co- sputtering for hydrogen gas sensing applications. The effect of annealing Pt/ ZnO/pt sensor has been appeared to have lower operation temperature and enhanced sensitivity.

Acknowledgements

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References

[1] J. Huang, Q.Wan, Sensors, 12 (2009) 9903-9924.

[2] N.H. Al-Hardan, MJ. Abdullah, A. Abdul Aziz, Int. J Hydrogen Energy, 35 (2010) 4428-4434.
[3] B.L. Zhu, D.W. Zeng, J. Wu1, WL. Song, CS. Xie, J. Mater Sci Mater Electron, 14 (2003) 521-526.
[4] D. Mishra, A. Srivastava, A. Srivastava, RK. Shukla, Appl Surf Sci, 255 (2008) 2947-2950.
[5] Choopun Supab, Hongsith Niyom, Mangkorntong Pongsri, Mangkorntong Nikorn, Physica, E 39 (2007) 53-56.
[6] D. F. Paraguay, M. Miki-Yoshida, J. Morales, J. Solis, L. W. Estrada, Thin Solid Films 373 (2000) 137-140.
[7] Hsueh Ting-Jen, Hsu Cheng-Liang, Sens Actuators, B131 (2008) 572-576.
[8] C. Han, S. Han, S.P. Khtkar, Sensors 6 (2006) 492–502.
[9] L. Boon-Brett, J. Bousek, G. Black, P. Moretto, P. Castello, T. Hubert, U. Banach, Int J Hydrogen Energy, 35, 1 (2010) 373–384.
[10] C.A. Grimes, K.G. Ong, O.K. Varghese, X. Yang, G. Mor, M. Paulose, E. C. Dickey, C. Ruan, M. V. Pishko, J. W. Kendig, A.J.Mason, Sensors, 3(2003) 69-82.
[11] V. Aroutiounian, Int J Hydrogen Energy, 32 (2007) 1145–1158.
[12] S. Fardindoost, A. Zad, F. Rahimi, R Ghasempour, Int J Hydrogen Energy, 35 (2010) 854–860.
[13] A.Z. Adamyan, Z.N. Adamyan, V.M. Aroutiounian. Int J Hydrogen Energy, 34 (2009) 8438–43.
[14] N. Van Hieu, N.Duc Chien, Physica B: Condensed Matter, 403 (2008) 50–56.
[15] O. Lupan, G. Chai, L.Chow, Microelectronics J, 38 (2007) 1211–6.
[16] J.B.K. Law, J.T.L. Thong, Nanotechnology, 19 (2008) 205502.
[17] G. Sberveglieri (Ed.), Gas sensors, Principles, Operation and Developments, Kluwer Academic Publications;(1992)p. 104.
[18] F. Zhiyong, L.G. Jia, Appl. Phys. Lett., 86 (2005) 123510.
[19] Y.I. Alivov, A.V. Chernykh, M.V. Chukichev, R.Y. Koroptkov, Thin Solid Films, 473 (2005) 241.
[20] S.M. Sze, "Semiconductor devices. Physics and technology", New York: Wiley; (1985) p. 179.
[21] V. Khranovskyy, J. Eriksson, A. Lloyd-Spetz, R. Yakimova, L. Hultman, Thin Solid Films, 517 (2009) 2073–2078.
[22] A. Gurlo, R. Riedel, Angew. Chem. Int. Ed., 46 (2007) 3826.
[23] J.N. Zemel, Thin Solid Films, 163 (1988) 189.
[24] B. Kamp, R. Merkle, J. Maier, Sensors and Actuators, B 77 (2001) 534-542.