IJE TRANSACTIONS B: Applications Vol. 27, No. 5, (May 2014) 757-762

International Journal of Engineering

Journal Homepage: www.ije.ir

Synthesis of Zinc Oxide Nanostructured Thin Film by Sol-gel Method and Evaluation of Gas Sensing Properties

M. R. Vaezi*, M. Zameni

Division of Nanotechnology and Advanced Materials, Materials Energy Research Center, Karaj, Iran

PAPER INFO

Paper history:
Received 22 July 2013
Received in revised form 20 October 2013
Accepted 07 November 2013

Keywords:
ZnO
Thin Film
Nanostructure
Sol Gel
Gas Sensor

ABSTRACT

Ethanol sensitivity of zinc oxide (ZnO) thin film has been studied in present work. Semiconductor thin films of zinc oxide (ZnO) were deposited onto soda lime glass substrates by the sol–gel method and dip-coating technique. The ZnO sol was synthesized by dissolving zinc acetate, Zn $(CH_3COO)_2.2H_2O$ in ethanol, and then adding triethanolamin (TEA). The as-coated films were preheated at 150 ºC for 10 min and annealed at 500 ºC for 1 h in air ambiance. Zinc oxide thin films were analyzed by field emission scanning electron microscopy (FE- SEM) and X- ray diffraction (XRD). In addition, Gas sensitivity of the zinc oxide thin film was determined by electrical sheet resistance measurements. The sensitivity to ethanol was remarkable and response and recovery time were only 8 sec, and 4 sec, respectively.

doi: *10.5829/idosi.ije.2014.27.05b.11*

1. INTRODUCTION

Chemical sensors with metal oxides as sensing material have been around for a long time as a low cost alternative for gas detection devices. Recent advances in nanotechnology and nonmaterial have fostered fabrication techniques that can be harnessed to increase the response and performance of these materials [1, 2]. This is because their performance is governed by the exposed surface area; the gas sensing mechanism being due to reactions that occur at the sensor surface. Thus, increasing the active surface area will likely increase the sensor performance [3].

Recently, nanostructures materials such as nano rods, tetra pods [4], or nanoparticles are used as gas sensors. However, still the thin film form is expected to be most effective and inexpensive way to obtain a large area coating for gas sensors. These nano layers have been produced by different chemical routs like spray paralysis, two stage chemical deposition (TSCD) chemical bath deposition (CBD), and sol gel processes. Within these methods, chemical methods like (CBD), (TSCD) and specially sol gel process are useful methods because they are inexpensive and quite simple methods. Among the chemical methods, sol gel process is the best technique. There are many advantages to sol gel processing such as good uniformity, simplicity of composition control, low processing temperature, large area coating, low equipment cost and good electrical and optical properties [5].

As gas sensor material, ZnO can be used to detect reducing gases (CO and H_2) [6], O_2 [3], O_3 or humidity. Recently, nano crystalline ZnO gas sensors have attracted more interest due to their better properties of detecting pollutants, toxic gases, alcohols [7] and food freshness, especially fish freshness, or as gas-sensing films integrated on one chip to make an "electronic nose" [8].

Ethanol (C_2H_6O) has widespread use as a solvent intended for human contact or consumption, including scents, flavorings, colorings, and medicines. However, long term use can result in serious liver damage. Thin film ZnO gas sensors can help us to detect even 1% vol ethanol at about 200˚C [9].

In this paper, an Ethanol sensor based on zinc oxide (ZnO) thin film can be produced with sol gel method and its gas sensing properties are studied.

*Corresponding Author Email: m_r_vaezi@merc.ac.ir (M. R. Vaezi)

2. EXPERIMENTAL

Zinc acetate ($Zn(CH_3COO)_2).2H_2O$ (Merck, 99.5%) was first dissolved in ethanol and triethanolamin (TEA) solution at 60 °C. The concentration of zinc acetate was kept at 0.5 $mol.L^{-1}$ and the molar ratio of TEA to zinc acetate was 1:1. The solution was stirred at 60 °C for 120 min until it became clear and homogeneous. The soda lime glass was used as substrate material. It was washed with water and ethanol in an ultrasonic bath and finally washed with deionized water and then dried in a hot air stream. The glass sheets then were dipped into the solution and withdrawn at the rate of 6 cm/min. The coated substrate was dried at 65 °C for 30 min in air and then dipped into the solution again. A pre- annealing operation was also carried out at 150 °C for 30 min and then kept at 500 °C for 1 hr. [5]. The X-ray diffraction (XRD) patterns of the samples were recorded at room temperature using a Unisuntis (XMD 300), with CuK_α radiation. The microstructure of the layers was investigated by FE- SEM. The specimens were coated previously with a thin (around 20 nm) gold layer, which was sputtered on top of the samples to avoid charging effects. Specimens were observed at accelerating voltages (< 20 kV) using Hitachi-S416 Japan field emission scanning electron microscope.

The measurement of gas sensing of ZnO layer was performed via gas sensing instrument made by the authors. Two electrodes of 2×4 mm^2 were deposited on each side of sensitive material (ZnO thin film coated on the substrate). Thin Pt wires were cemented to this area by conductive epoxy resin (Duralco- 124). The substrate was then attached to a temperature- controlled micro-heater, and was mounted on a refractory stand, so that the temperature of the substrate could be adjusted in the 25- 450°C temperature range. A sensor probe was formed by mounting the sample on a thick- walled borosilicate glass tubing, through which two insulated connection cables were guided to the temperature control unit and the impedance measurement device, respectively. A load resistor, R_L was connected in series with the sensor element, R_S. Then, a constant AC voltage (10 v, 80 HZ) was applied across R_L and R_S. Test gases were passed into the borosilicate glass tank. The resistance of the sensor was obtained by measuring the voltage drop, V_S across the sensor element. A chromel- alumel thermocouple (TC) was placed on the device to indicate the operating temperature. The details of construction and schematic illustration of the fabricated gas sensor have been reported in the other work [10].

3. RESULTS AND DISCUSSION

In the present work, XRD pattern of ZnO Nano powder is conformed to the standard one (Figure 1). In addition, the optimum temperatures for heat treatment of ZnO nanopowder were determined from Simultaneous Thermal Analysis**,** STA (Figure 2). Therefore, the temperatures of 65 °C for drying, 150 °C for pre-annealing operation and then 500 °C were chosen to final sintering.

Furthermore, the particle size of produced ZnO layer is about 70 nm and its thickness is 400-500 nm (see Figures 3 and 4). It is necessary to note that the thickness of films was controlled by the number of dipping and after 5 times of dipping, the thickness can be reached to 400- 500 nm.

After checking the characterization of produced layer, it was exposed to ethanol gas for studying of sensing behavior. At first it is necessary to explain about sensing mechanism in brief. These materials are characteristically n-type semiconductors due to non-stoichiometry associated with oxygen vacancy and/or metal excess acting as donor states providing conduction electrons.

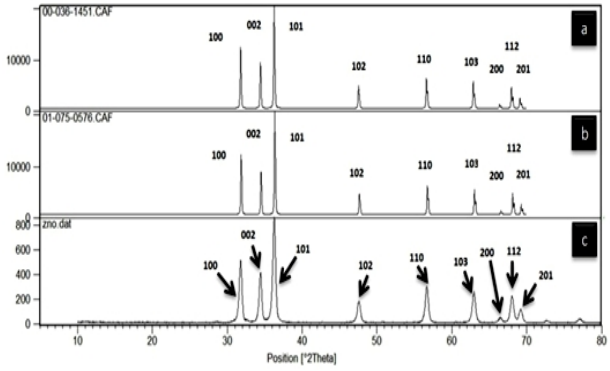

Figure 1. XRD reference patterns of ZnO (a & b) and ZnO Nano powder synthesized via sol- gel processing (c).

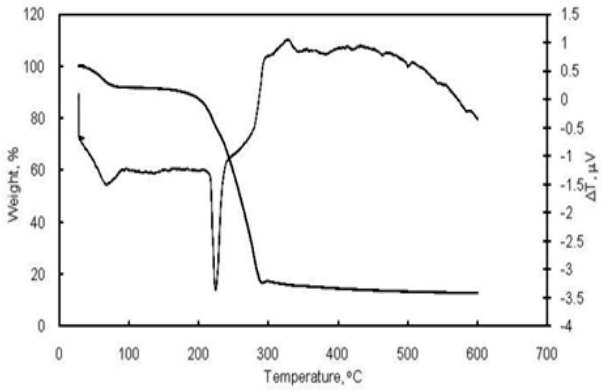

Figure 2. STA (STA 1640) result of ZnO nanopowder for determine the heating rate and optimum temperatures of heat treatment.

However, the overall surface resistance of such films is greatly influenced by chemisorption (chemical absorption) of oxygen from air on the surface and at the grain boundaries. The chemisorbed oxygen traps conduction electrons and remains as negatively charged species (O_2 -, O- or O_2- depending on temperature) on the surface [11]. The process results in an increase of surface resistance. In presence of a reducing gas, the trapped electrons are released due to reaction between the gas molecules and the negatively charged chemisorbed oxygen species resulting in a decrease in resistance of the material. When the gas is removed from the sensor environment, the resistance again increases and the material recovers to original resistance [12]. The sensing mechanism of ethanol is closely related to its decomposition and/or oxidation reaction. Jinkawa et al. [13] reported that the decomposition of ethanol at elevated temperatures depended on the acid–base properties of the oxide catalyst used [14]

$$C_2H_5OH\ (g) \rightarrow CH_3CHO\ (g) + H_2\ (g) \quad \text{(Basic oxide)} \tag{1}$$

$$C_2H_5OH\ (g) \rightarrow C_2H_4\ (g) + H_2O\ (g) \quad \text{(Acidic oxide)} \tag{2}$$

Since ZnO is an acidic oxide, second equation is correct in this research. Therefore, it can be shown that the sensitivity to ethanol gas, increases with temperature, and also with concentration rising. The best sensitivity also belongs to about 300 °C operation temperature. These desirable properties are related to homogeneity of structure, nano size of crystallites and also film slightness. When the conduction width is smaller than $2LD$[2], the space charge layers from the opposite surfaces overlap to form a higher-resistance ohmic path through the depleted zone [11]. This is often found in a less sintered ceramic with "closed necks" and in thin films and pressed ceramics with Nano-crystallites. In this case, flat-band conditions are fulfilled to a good approximation and the conductance, G, is determined by the activation of electrons from the surface states to the conduction band edge at the surface (surface-trap-limited conduction) expressed as Equation (3):

$$G \propto exp[-(Ec - Es)S/kT] \tag{3}$$

where $(Ec - Es)S$ corresponds to the difference between the conduction band edge at the surface and the surface state energy level. The sensitivity is achieved by the modulation of the surface conduction band energy, resulting from the direct change in the occupancy of surface states [15].

[2] Debye length of electron : $LD = \sqrt{\varepsilon_s kT/(e^2 n_b)}$ where ε_s, e and n_b are the permittivity of the oxide, the elementary electron charge and the bulk electron density, respectively

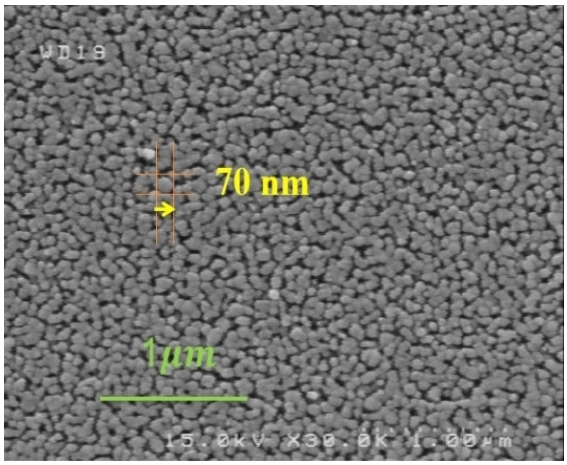

Figure 3. FE- SEM micrograph of ZnO Nano layer.

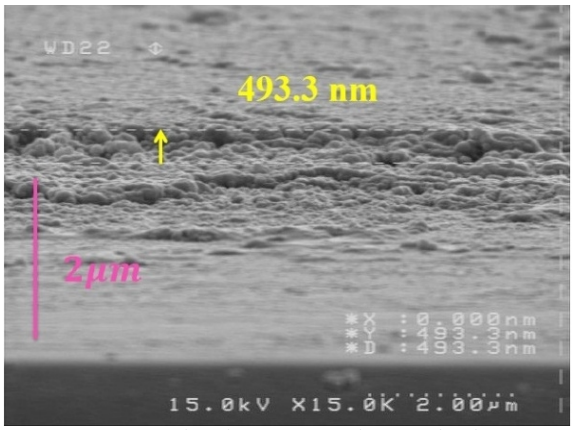

Figure 4. Cross sectional FE- SEM micrograph of ZnO Nano layer. The thickness of layer is about 400- 500 nm.

The responses of the ZnO- based nano layer sensor to ethanol have been measured at different concentrations ranging from 500 to 2000 ppm and at operating temperature in the range from 125 to 425 ºC to investigate the gas sensing properties. Figure 5 shows the variation of sensitivity to 1000 ppm of ethanol with operating temperature for ZnO nano layer samples. It is observed that the sensitivity of ZnO nano layer increases with temperature and attains a maximum at 290 ºC, and again decreases with further increase in the temperature. Working temperature is one of the most important parameters for gas sensors. The conventional gas sensors based on ZnO materials operate at the temperature region from 250 to 400 ºC [16].

The sensitivities of a sample device to various ethanol concentrations were measured. The results are presented in Figure 6, indicating an almost linear increase in sensitivity with increasing target gas concentration up to 2000 ppm at optimum temperature of sensor.

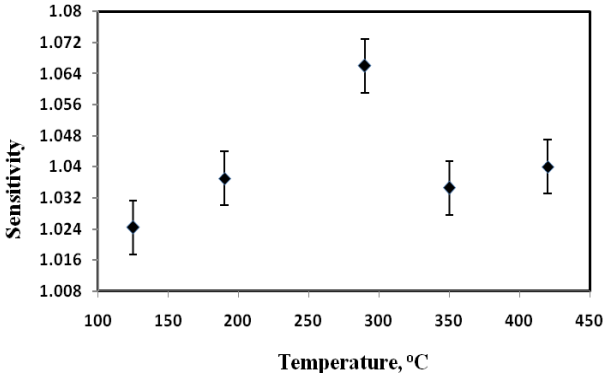

Figure 5. Variation of ZnO sensitivity vs. the temperature.

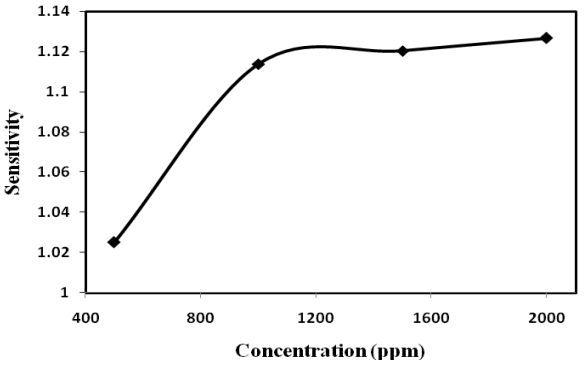

Figure 6. Variation of ZnO sensitivity vs. gas concentration at optimum temperature.

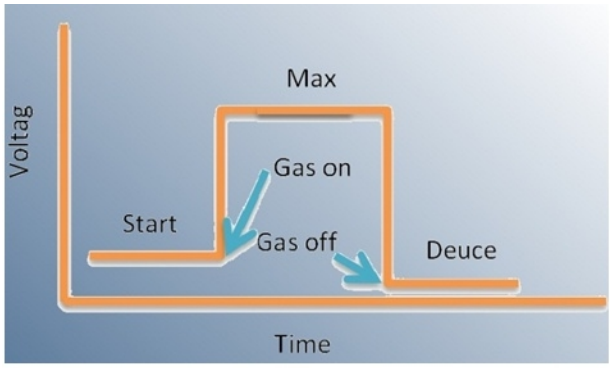

Figure 7. Dynamic response of ZnO Nano layer Gas sensing diagram

A saturation of sensitivity is observed for higher concentration levels, as reported by others [7]. Response and recovery time are two other most important property of gas sensors. The response and recovery time for ZnO thin film are 8 sec. and 4 sec., respectively. Some equations can help us to reach these valuable properties.

As shown in Figure 7, the sensor resistance increases when exposed to gas ambient. The response time, defined as the time needed to reach 90% of the final steady value of the sensor resistance after the test gas injection, can discover from the Equations (4-7):

$$V_{Start} - V_{Max} = V_1 \quad (4)$$

$$V_1 \times 90\% = V_2 \quad (5)$$

$$V_2 + V_{Start} = V_{90\%} \quad (6)$$

$$t_{V_{90\%}} - t_{V_{Start}} = t_{V_{Res}} \quad (7)$$

where, V_{start} and V_{Max} are shown in Figure 7 and t_{VRes} is the response time.

The recovery time, defined as the time needed to return to 90% of the initial steady value of the sensor-resistance after the chamber was opened up, can also discover from the Equations (8-11):

$$V_{Max} - V_{Deuce} = V_3 \quad (8)$$

$$V_3 \times 10\% = V_4 \quad (9)$$

$$V_4 + V_{Deuce} = V_{10\%} \quad (10)$$

$$t_{V_{10\%}} - t_{V_{Max}} = t_{V_{Rec}} \quad (11)$$

where, V_{Max} and V_{Deuce} are shown in Figure 7 and t_{VRec} is the recovery time. In the Equations (4- 11), t and V are referred to time and voltage, respectively.

4. CONCLUSION

The result of this investigation shows that a desirable zinc oxide (ZnO) thin film gas sensor can be produced with cheap price sol gel method and simple dip coating techniques. Moreover, this thin layer display an acceptable sensing behavior at 200 ºC and very short response and recovery time about 8s and 4s, respectively. This is related to its very homogenate structure and also its very thin depth.

5. REFERENCES

1. Kumar, R. R., Grabowska, J., Mosnier, J., Henry, M. and McGlynn, E., "Morphological control of ZnO nanostructures grown on silicon", in Integrated Optoelectronic Devices, International Society for Optics and Photonics. (2007), 64741I-64741I-5.
2. Sberveglieri, G., Baratto, C., Comini, E., Faglia, G., Ferroni, M., Ponzoni, A., and Vomiero, A., "Synthesis and characterization of semiconducting nanowires for gas sensing", ***Sensors and Actuators B: Chemical***, Vol. 121, No. 1, (2007), 208-213.
3. Eriksson, J., Khranovskyy, V., Söderlind, F., Käll, P.-O., Yakimova, R., and Spetz, A. L., "ZnO nanoparticles or ZnO

films: A comparison of the gas sensing capabilities", ***Sensors and Actuators B: Chemical***, Vol. 137, No. 1, (2009), 94-102.

4. Pawar, R., Shaikh, J., Suryavanshi, S. and Patil, P., "Growth of ZnO nanodisk, nanospindles and nanoflowers for gas sensor: pH dependency", ***Current Applied Physics***, Vol. 12, No. 3, (2012), 778-783.
5. Hu, W., "Improved photocatalytic performance of ZnO prepared by sol–gel method with the assistance of CTAB", ***Materials Letters***, Vol. 91, No., (2013), 301-303.
6. Lim, S. K., Hwang, S.-H., Kim, S. and Park, H., "Preparation of ZnO nanorods by microemulsion synthesis and their application as a CO gas sensor", ***Sensors and Actuators B: Chemical***, Vol. 160, No. 1, (2011), 94-98.
7. Ge, C., Xie, C. and Cai, S., "Preparation and gas-sensing properties of Ce-doped ZnO thin-film sensors by dip-coating", ***Materials Science and Engineering: B***, Vol. 137, No. 1, (2007), 53-58.
8. Musat, V., Rego, A., Monteiro, R. and Fortunato, E., "Microstructure and gas-sensing properties of sol–gel ZnO thin films", ***Thin Solid Films***, Vol. 516, No. 7, (2008), 1512-1515.
9. "www.wikipedia.com. "
10. Vaezi, M., "SnO_2/ZnO double-layer thin films: A novel economical preparation and investigation of sensitivity and stability of double-layer gas sensors", ***Materials Chemistry and Physics***, Vol. 110, No. 1, (2008), 89-94.
11. Schierbaum, K. D., Kirner, U. K., Geiger, J. F. and Gopel, W., "Schottky-barrier and conductivity gas sensors based upon Pd/SnO_2 and Pt/TiO_2", ***Sensors and Actuators B: Chemical***, Vol. 4, No., (1991), 87- 94.
12. Mitra, P. and Mukhopadhyay, A., "ZnO thin film as methane sensor", ***Bull. Polish Acad. Sci. Tech. Sci***, Vol. 55, No., (2007), 281-285.
13. Jinkawa, T., Sakai, G., Tamaki, J., Miura, N. and Yamazoe, N., "Relationship between ethanol gas sensitivity and surface catalytic property of tin oxide sensors modified with acidic or basic oxides", ***Journal of Molecular Catalysis A: Chemical***, Vol. 155, No. 1, (2000), 193-200.
14. Kim, K.-W., Cho, P.-S., Kim, S.-J., Lee, J.-H., Kang, C.-Y., Kim, J.-S., and Yoon, S.-J., "The selective detection of C2H5OH using SnO_2-ZnO thin film gas sensors prepared by combinatorial solution deposition", ***Sensors & Actuators: B. Chemical***, Vol. 123, No. 1, (2007), 318-324.
15. Park, C. O. and Akbar, S., "Ceramics for chemical sensing", ***Journal of materials science***, Vol. 38, No. 23, (2003), 4611-4637.
16. Lee, D.-S., Rue, G.-H., Huh, J.-S., Choi, S.-D. and Lee, D.-D., "Sensing characteristics of epitaxially-grown tin oxide gas sensor on sapphire substrate", ***Sensors and Actuators B: Chemical***, Vol. 77, No. 1, (2001), 90-94.

Synthesis of Zinc Oxide Nanostructured Thin Film by Sol-gel Method and Evaluation of Gas Sensing Properties

M. R. Vaezi, M. Zameni

Division of Nanotechnology and Advanced Materials, Materials Energy Research Center, Karaj, Iran

P A P E R I N F O

Paper history:
Received 22 July 2013
Received in revised form 20 October 2013
Accepted 07 November 2013

Keywords:
ZnO
Thin Film
Nanostructure
Sol Gel
Gas Sensor

چکیده

در این مقاله، حساسیت لایه نازک اکسید روی به گاز اتانول مورد بررسی قرار گرفته است. لایه های نازک نیمه هادی اکسید روی بر روی شیشه سودالایم به روش سل ژل و با استفاده از تکنیک غوطه وری لایه نشانی شده است. سل اکسید روی با حل کردن استات روی در اتانول و سپس افزودن تری اتانول آمین سنتز شد. لایه های بدست آمده در دمای ۱۵۰°C به مدت ۱۰ دقیقه خشک شده و سپس در دمای ۵۰۰ °C به مدت ۱ ساعت در هوا آنیل شدند. لایه های نازک اکسید روی توسط میکروسکپ الکترونی نشر میدانی و تفرق اشعه ایکس مورد آنالیز قرار گرفتند. همچنین، حساسیت گازی لایه های نازک اکسید روی با اندازه گیری های مقاومت الکتریکی صفحه ای تعیین شد. در این راستا، حساسیت مقدار قابل ملاحظه ای بود و زمان پاسخ و بازیابی به ترتیب ۸ و ٤ ثایه بدست آمد.

doi: *10.5829/idosi.ije.2014.27.05b.11*