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

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**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(CH₃COO)₂·2H₂O 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.

**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 routes 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 H₂) [6], O₂ [3], O₃ 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 (C₂H₅O) 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.

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2. EXPERIMENTAL

Zinc acetate (Zn (CH$_3$COO)$_2$.2H$_2$O (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$_\alpha$ 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 microheater, 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).](image)

![Figure 2. STA (STA 1640) result of ZnO nanopowder for determine the heating rate and optimum temperatures of heat treatment.](image)
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$_2^{2-}$ 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].

\[
\begin{align*}
C_2H_5OH (g) & \rightarrow CH_3CHO (g) + H_2 (g) \\
& \text{(Basic oxide)}
\end{align*}
\]

\[
\begin{align*}
C_2H_5OH (g) & \rightarrow C_2H_4 (g) + H_2O (g) \\
& \text{(Acidic oxide)}
\end{align*}
\]

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):

\[
G \propto \exp[-(E_c - E_s)S/kT]
\]

where $(E_c - E_s)S$ 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].

Debye length of electron : $LD = \sqrt{\varepsilon_0 kT/\varepsilon^2 n_b}$ where $\varepsilon_0$, $e$ and $n_b$ are the permittivity of the oxide, the elementary electron charge and the bulk electron density, respectively.
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):

\[ V_{\text{start}} - V_{\text{Max}} = V_1 \]  
\[ V_1 \times 90\% = V_2 \]  
\[ V_2 + V_{\text{start}} = V_{90\%} \]  
\[ t_{\text{Rec}} = t_{\text{start}} - t_{\text{Rec}} \]  

where, \( V_{\text{start}} \) and \( V_{\text{Max}} \) are shown in Figure 7 and \( t_{\text{Rec}} \) 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):

\[ V_{\text{Max}} - V_{\text{Decay}} = V_3 \]  
\[ V_3 \times 10\% = V_4 \]  
\[ V_4 + V_{\text{Decay}} = V_{10\%} \]  
\[ t_{\text{Rec}} = t_{\text{Max}} - t_{\text{Rec}} \]  

where, \( V_{\text{Max}} \) and \( V_{\text{Decay}} \) are shown in Figure 7 and \( t_{\text{Rec}} \) 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 °C 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

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