Fabrications of NO Gas Sensors Based on ZnO Nanorod Thin Films

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***Abstract*—Nitric oxide (NO) gas is extremely dangerous and can cause health problems such as respiratory infections, poisoning and lung damage. In addition NO gas is colorless and odorless. In this study a sensors based on thin films of zinc oxide (ZnO) nanorod structure is fabricated using dip coating method and Chemical Bath Deposition (CBD) to detect NO gas. The results of the characterization of SEM, EDS, and XRD showed that thin films of ZnO nanorod structures have been successfully fabricated on an alumina substrate. The sensors have good ability to measure changes in the concentration of NO gas. The optimum working temperature of the sensors is 300 ℃ with a sensitivity of 90.62%. The sensor can distinguish the concentration of NO gas at a concentration of 10ppm, 30ppm, 50ppm, and 70ppm with a sensitivity of 90.62% at the largest and the fastest response time of 8 minutes at a concentration of 70ppm. Moreover the sensor has the fastest recovery time of 8 minutes at a concentration of 10ppm.**

***Index Terms*—zinc oxide, nitric oxide, gas sensor, thin films, nanorod**

I. Introduction

In most country, the environmental protection is toward the regulation, measurement and control of nitric gases in atmosphere. It is well known that among the ambient air pollutants, NO is one of the most dangerous gases both environmentally and from a human perspective even at low concentrations. Emissions of nitric oxide contribute to a variety of environmental problem, including photochemical smog, acid deposition, and visibility impairment through particulate nitrates [1]. Nitric oxide (NO) gas is extremely dangerous and can cause health problems such as respiratory infections, poisoning and lung damage [1].

Recently, most of the researchers use metal oxide semiconductor materials such as ZnO, SnO_2, TiO_2, Fe_2O_3, In_2O_3, and WO_3 to develop sensor gas equipments [2] Among those semiconductor oxides, thin film ZnO is one of the most popular because its unique properties to produce high electrical conductivity [3]. The ZnO is one of the most promising materials for gas sensors application because its high thermal and chemical stability, high compatibility with semiconductor processing and low cost. ZnO is one of n-type semiconductor with direct band gap and large band gap energy of 3.37eV at room temperature [2]. Nowadays, the problems of ZnO gas sensor performance are the high operating temperature and relatively low sensitivity. In recent development of sensor materials, the modifications on nano structure have been yield better sensing performance [3]. In the present paper, the high sensitive ZnO nanorod thin films sensor for NO gas detection as are investigated. The ZnO sensors are able to detect as low as 10 ppm of NO gas.

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II. Experimental

A. Material synthesis

In this study, $(Zn(NO_3)_2.4H_2O)$zinc nitrate tetrahydrate as precursor, ethanol and water as a solvent, and Hexamethylene tetramine (HMTA) as the surfactant will be mixed to make a homogeneous solution. Hexamethylene tetramine is a non-ionic compound that has a cyclic structure and can serve as a base compound for metal ions [4]. The resulting mixed of dissolution process will be occured chemical reaction to produce $Zn(OH)_2$. After that, the homogeneous solution was deposited on the surface of the substrate.

The synthesis processes of the ZnO nanorod thin films are shown in the Fig. 1. The reaction occurs when the dissolution of precursors have reactions as stated in equations (1) until (3). In reaction (1), the Zn^{2+} is formed, which then reacts with hydroxide ions from the HMTA decomposition resulted from the reactions on equations (2) and (3). At reaction on equations (4), it can be seen that the reaction of Zn^{2+} and hydroxide ions will produce $Zn(OH)_2$. The reactions on equation (5) and (6) occurred when the deposition process was performed on the substrate, which eventually form a bond of ZnO on the substrate.

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^- \quad (1)$$

$$(CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \quad (2)$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^- \quad (3)$$

$$2OH^- + Zn^{2+} \rightarrow Zn(OH)_2 \quad (4)$$

$$Zn(OH)_2 + Zn(OH)_2 \rightarrow 2Zn\text{-}O\text{-}Zn + 2H_2O \quad (5)$$

$$2Zn\text{-}O\text{-}Zn + O_2 \rightarrow 4ZnO(s) \quad (6)$$

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The process of seed formation is created by the dip-coating method to yield seed structure evenly. The dip coating method has been chosen since this technique is considered quite simple, inexpensive, and low time consuming. It is well experienced that by producing the seed layer, the films have higher chance to form the nanorod structure growth [5], [6]. After the ZnO seed is formed, then the next step to do is to make a homogeneous solution using Chemical bath deposition (CBD) [2]-[7]. The precursor solutions were made by a certain amount of concentration as follow. The solution was then stirred using a magnetic stirrer for 30 minutes at room temperature to produce a homogeneous solution.

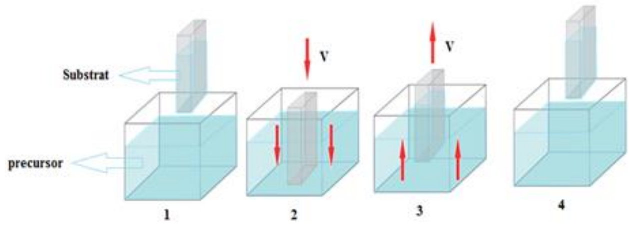

Figure 1. Dip coating process ilustration

After the seed is formed, the substrate were soaked in the solution and put into a furnace at the temperature of 80℃ for 6 hours. Once a thin film is formed then the calcination is treated to the thin films to remove the impurities compounds in the substrate. The calcination of the resulting thin films has been treated by heating a thin film of ZnO substrate in the furnace at 350℃ for 30 minutes.

B. *Gas Target Detection*

The working principle of gas sensors with ZnO semiconductor nano structure materials are based on the changes in the physical and chemical properties of the material when exposed to the targeted gas. When the semiconductor material exposed to the target gas, the chemical reaction will be occurred. This chemical reaction will then cause a material change of physical phenomena such as electrical conductivity and resistance. This value was then measured in the detection as a function of the target gas. In environments ambient, the oxygen (O_2) gas excess NO reacts with oxygen to form NO_2 [8], [9].

$$2NO_{gas} + O_{2gas} \rightarrow 2NO_{2gas} \quad (7)$$

Therefore here the gas that is used to represent the state of the ambient was N_2. When the ZnO nano structure thin films are exposed to the N_2, there is no reaction occurs because the N_2 gas is actually an inert gas [9], [10].

$$NO_{gas} + e^- \rightarrow NO^-_{ads} \quad (8)$$

$$2NO^-_{ads} \rightarrow 2O^-_{ads} + N_{2gas} \quad (9)$$

$$2NO^-{}_{+} e^- \rightarrow O^-_{ads} + N_2O \quad (10)$$

The NO gas was partially reduced on the surface of ZnO material as stated in the equation (8), (9) and (10). At the time of NO gas presented in the ZnO nano structure thin films, the NO gas molecules will interact with the surface of a ZnO thin films and the Zn will capture the electrons from the atoms contained in the ZnO surface. This reaction leads to a decrease in the concentration of electrons in the conduction band of ZnO resulting in a decrease in conductivity and increase the resistance of the gas sensor further [11], [12].

III. Results and Analysis

A. *Material Characterization*

The resulting ZnO nanorod thin films were characterized to determine the composition and morphology of the films. The ZnO thin films that have been deposited onto the substrates were characterized using Scanning Electron Microscopy (SEM) to see the structure and morphology of the thin films. The Energy Dispersive X-Ray Spectroscopy (EDS) is also used to determine the composition of substances or elements formed of the thin films. The resulting thin films have been treated by X-Ray Diffraction (XRD) to investigate the phase and crystal formed of the thin films.

The characterization of X-Ray Diffraction (XRD) on the resulting ZnO thin films were investigated both for the films synthesized using dip-coating method and using the chemical bath deposition (CBD). This characterization is done using an X-ray diffractometer, X-Ray Analytical Phillips PW1710 type generator voltage of 40kV generator current of 30mA. The diffraction pattern obtained using Cu radiation (=1.54060 Å $\lambda1$ and $\lambda2$=1.54439 Å).

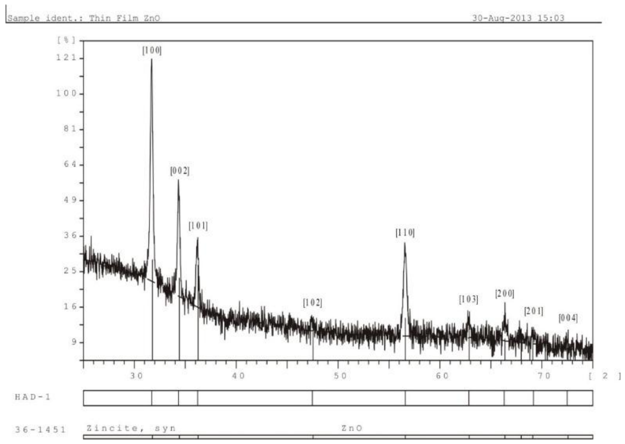

Figure 2. The X-Ray Diffraction (XRD) measruements of the ZnO nanorod thin films

The crystalline phase of the material that is formed on the substrate showed a similar pattern with the crystal phase of ZnO as shown in the Fig. 2. It can be seen from the existing peaks that the crystal orientation of the material is accordance with Zincite crystal phase. The peak of the XRD measurements that is captured from the diffraction are as follow: [1 0 0], [0 0 2], [1 0 1], [1 0 2], [1 1 0], [1 0 3], [2 0 0], [2 0 1], and [0 0 4]. The 2θ degrees are at 320º, 340º, 360º, 480º, 570º, 630º, 660º, 690º, and 720º. There are 9 peaks were recorded at the XRD measurements where the strongest intensity have been investigated on the [1 0 0] at 2θ =320º.

The data of the crystal phase of resulting ZnO nanorod thin films have been analyzed and compared to the database provided by the Joint Committee on Powder Diffraction Standards (JCPDS). According to the JCPDS database, the crystalline phase of the after synthesized ZnO nanorod thin films is the wurtzite hexagonal structure. It can be seen on the XRD result that the ZnO structure has been successfully established on the thin films.

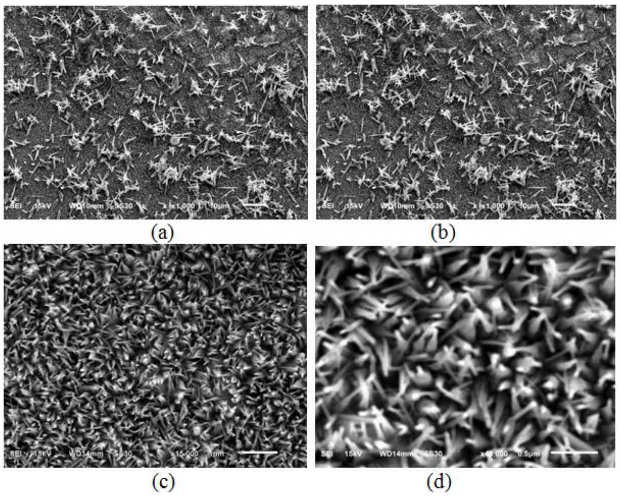

Figure 3. The SEM measurements of ZnO nanorod thin films with: a) magnification of 1.000X, b) magnification of 10.000X, c) magnification of 15.000X, and d) Magnification of 40000X

The Fig. 3 is the measurement data of SEM with various magnifications. The Fig. 3 shows the nanostructure of the ZnO thin films are successfully formed. The morphology of the resulting ZnO thin films is nanorod structure which can be seen clearly from the Fig. 3. (d) especially in the bigger magnifications. The nanorod structure has been successfully growth on the samples prepared by dip-coating method and the CBD using HMTA as a surfactant. The SEM measurements also recored that the size of the rod is almost homogenous in nanoscale. This is presumably due to the appropriate process of the CBD technique used on the samples to growth the thin film.

B. *The Effect of Operating Temperature to the Sensing Performance*

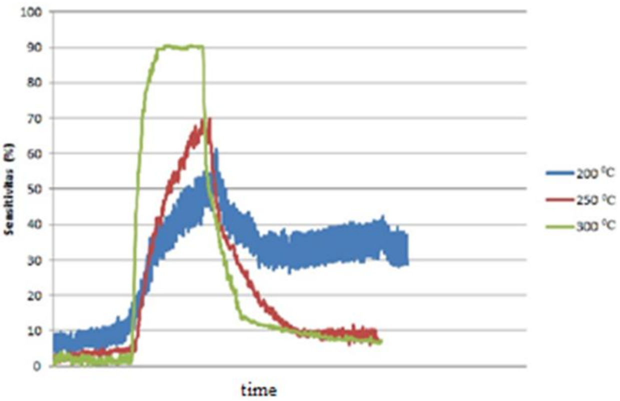

Figure 4. The dynamic response of the ZnO nanorod thin films sensors upon the exposure of NO gas in various temperatures

The Fig. 4 displays the data obtained from the sensing performances test of the NO gas in different operating temperature. The tests were conducted at the operating temperature of 200 ℃, 250 ℃ and 300 ℃. The investigations are measured by exposing the target gas (NO) with a saline concentration of 70ppm respectively for 30 minutes. It can be seen on the Fig. 4 that the best response among the three temperatures is at an operating temperature of 300 ℃. It can be seen from the Fig. 4 that the sensitivity response of the sensor increases as the increasing of operating temperature in the range of the tested temperature from the 200 ℃ to the 300 ℃. The sensor has longer response time at lower temperature, which is the evidence that at lower temperature the ZnO nanorod structure thin films exhibit fewer electrons to change the resistance of the sensors. In contrary, the response time of the sensors has the fastest response time at the operating temperature of 300 ℃.

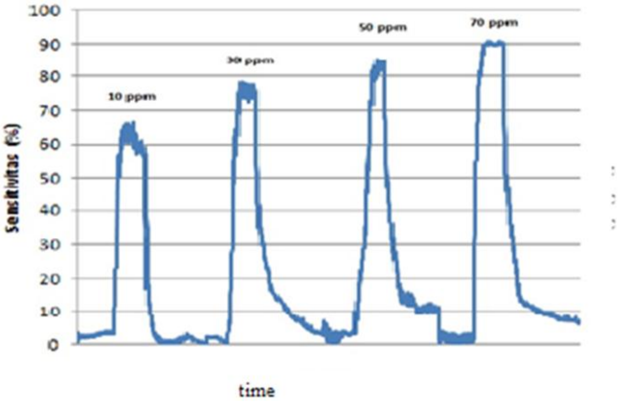

Figure 5. The dynamic response of ZnO nanorod thin films in different concentration of NO gas

The highest sensitivity obtained at the operating temperature of 300 ℃ with a value of 90.62% and the lowest sensitivity is obtained at an operating temperature of 200 ℃ with a value of 61.21%. As for the response of the sensor response time is also the best when the operating temperature of 300 ℃. It only takes about 8 minutes to reach the level of the state of 90% after NO gas presented. While the longest response time happens at the operating temperature of 200 ℃ with a time of 26 minutes. When the gas concentration increased the resistance change that occurs is also getting bigger. So sensitivity is also higher with higher concentrations.

IV. Conclusions

In conclusions, we successfully fabricated the ZnO nanorod thin films for nitric oxide gas sensor. The nanorod structure was successfully synthesized using combination of dip-coating and chemical bath deposition methods. The ZnO nanorod thin films, which its best sensitivity as much as 90.62% on 70ppm of NO gas and 300 ℃ of operating temperature (shown in Fig. 5).

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