The application of zinc oxide layer as ethylene sensor

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Abstract. As an emerging n-type semiconductor, ZnO has been widely applied in sensor area. In this study, we prepared an ethylene sensor using ZnO layer on FTO glass substrate. The seed layer was deposited using simple electrodeposition method using voltage of -1.1 V for 2 hours in cold bath (6°C). The ZnO layer was further grown using CBD technique at 90°C for 2 hours. In order to observe the effect of structural manipulation on the sensor performance, some of the ZnO layer samples were undergoing hydrothermal treatment at 100°C for 1 hour under 1 bar N₂ gas. After annealing process, all ZnO layers were exposed with 50 ppm ethylene gas in closed chamber. Based on the results, it is shown that the optimum ZnO layer has been successfully identified the ethylene gas in concentration of 50 ppm, with response value of 2.40% at 200°C.

1. Introduction
Sensor is an electronic circuit component, which can sense physical and chemical signals coming from a stimulant existing around precisely and can convert them into measurable quantities and generally, electrical signals. There are various sensors according to where they are used like biosensors, gas sensor, humidity sensor, pressure sensor, vibration sensor, temperature sensor, speed sensor, and magnetic field sensor [1]. Because it has been considered that advanced semiconductor technology allows the desired superior features for the sensors to be ensured, the use of especially metal oxide semiconductors as a sensing material has increased recently and this has positively contributed to development of sensors. Among the sensing materials, metal oxide semiconductors like ZnO, CdO, SnO₂, TiO₂, CuO, and WO₃ have become preferable than other sensor types due to their higher sensitivity and their ability in working under severe conditions and their longer lifecycle superior [1].

Of all available types of semiconductor sensors for different types of chemicals and biological toxins, ZnO-based sensors have gained extensive attention around the world. The presence of a good response rate towards the chemical toxins with outstanding selectivity and sensitivity makes it one of the most significant materials for preparing low cost sensors [2]. Being an n-type semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, the electron mobility in ZnO nanomaterials is enhanced [2]. In addition, ZnO nanomaterials have the advantages of a low cost of production, a harmless nature and a simple mode of large-scale production. Furthermore, ZnO nanomaterials are chemo-resistive in nature, and their sensing aptitude is principally restricted by the change in the chemical signal when the respective analyte molecules encounter its exterior surface [2].

In recent years, much attention has been given to ZnO-based nanostructures for sensing. The presence of the numerous properties of ZnO has been utilized for the development of effective and...
highly selective sensors [2]. Undoped and doped ZnO materials with different metals have been studies for sensor applications. To this date, the use of ZnO as a sensing material has been investigated for many sensors, e.g. humidity [3], formaldehyde [4], and SO₂ [5] sensor.

Ethylene is a small hormone in plant which controls the ripening process. Previously, Esser et al [6] has been investigating the role of carbon nanotube as an ethylene sensor in fruit ripening process. Inspired by Esser’s results, in this study, we prepared a ZnO layer which applied as a sensing material for ethylene gas. The ZnO layer was grown on conductive glass surface using simple electrodeposition process. The morphologies, optical, electrical, and structural properties of the ZnO layers were further investigated. Using the data, the correlation among the properties and sensing behavior were concluded afterward.

2. Experimental Methods

The synthesis procedure for fabricating ZnO nanorods was started firstly with preparation of substrates. The fluoride-doped tin oxide (FTO) glasses (Dyesol, Ω 7 ohm/m²) were cleaned using aquades, aceton and ethanol in ultrasonic cleaner for 480 seconds in each liquid. The cleaned glasses were dried and stored in a clean container until further use. The seed solution was prepared using 0.1 M zinc nitrate tetrahydrate (Zn(NO₃)₂.4H₂O/Zn-nitrate, Merck), hexamethylenetetraamine (C₆H₁₂N₂/HMTA, Merck) and dissolved in cold water (0°C) in a beaker glass, then aged for 1 hour. The electrodeposition system was constructed using FTO glass as the cathode and Cu metal as the anode. The experiment was conducted using voltage of -1.1 V for 2 hours in cold bath (6°C).

The ZnO layer on FTO glass was grown using chemical bath deposition (CBD) method afterwards. The seeded FTO glass was placed vertically in equimolar Zn-nitrate solution and HMTA 0.05 M at 90°C for 2 hours in the oven. After that, the FTO glass was washed using distilled water and dried in air. In order to observe the effect of structural manipulation on the sensor performance, some of the as-grown ZnO layer samples were undergoing hydrothermal (HT) treatment by placing the layer on top of boiling water in a reactor. The ZnO layer was placed upside down, facing the bottom of the reactor. This process was carried out used a closed reactor at 100°C for 1 hour under 1 bar nitrogen gas (N₂) pressure. The as-grown and HT ZnO layer samples were annealed at 200°C for 10 minutes after each processes of synthesis subsequently. The layers were further exposed to 50 ppm ethylene gas in closed chamber under 2 different temperatures, i.e. 100 and 200°C.

The morphology of the obtained ZnO nanorods was examined using field emission-scanning electron microscopy (FE- SEM, FEI Quantana 650), while the crystal structural information was gained using X-ray diffraction (XRD, Pan Analytical X-Pert Pro), and the optical properties were analyzed using diffuse reflectance (DRS) UV-Vis spectroscopy (Shimadzu 2450). The respective $E_g$ of the samples was determined by using Tauc equation.

3. Results and Discussion

SEM results for ZnO thin films on FTO glass are shown in figure 1. Most of the ZnO were grown in rod structure, with hexagonal cross-section. Hydrothermal (HT) method produces more variation of diameter nanorods than CBD (Figure 1). The average diameter of nanorods resulted from CBD process is 0.704 μm, while hydrothermal samples had an average diameter of 1.157 μm. From the cross-sectional view (Figure 2), it is revealed after CBD process, the ZnO layer experiences growth in different directions. Despite structures that grow on the z-axis (perpendicular), ZnO rods that grow in diagonal or horizontal direction is still visible in the structures. From the measurement, the thickness of ZnO after CBD was 1.98 μm. However, the thickness of ZnO layer after HT treatment was not convenient to determine. Figure 2.b. has revealed that after HT treatment, the vertical rod structure was collapsed, hence resulting a stack of ZnO rods. Thus, we can assume that using hydrothermal treatment may damage the rod structure, due to the pressure applied during the process.
Figure 1. Top view of ZnO layer on FTO substrate a) as-grown using CBD method, b) after hydrothermal treatment, with magnification of 10,000x.

Figure 2. Cross-sectional view of ZnO layer on FTO substrate a) as-grown using CBD method, b) after hydrothermal treatment, with magnification of 20,000x.

Diffractogram patterns of ZnO layer is presented in Figure 3. From the figure, it is shown that the diffractograms not only presenting ZnO peaks, but also the peaks for FTO substrate. The ZnO layer has a polycrystalline structure, which confirmed with ICSD number 98-018-0052. As seen in the patterns, there are some peaks having different orientations and, existence of the planes corresponding to the three different main peaks, which are (100), (002) and (101). In both samples, the most dominant peak for ZnO was measured at 2θ 31.67º, which correspond to (100) crystal plane. The weak peaks (102), (110), and (103) were also observed, in addition to, these three main peaks.

The crystalline size of the samples is determined using Debye–Scherrer relation [7]:

\[
D = \frac{0.9 \lambda}{\beta_{hkl} \cos \theta}
\]  

where D is the crystal size, \( \beta_{hkl} \) is the peak width of half maximum intensity, \( \theta \) is the diffraction angle and \( \lambda \) represents wavelength of the X-ray. From the calculation, it is obtained that the crystallite size for ZnO sample after CBD and HT treatment were 127.03 nm and 138.36 nm, respectively.

The optical behavior of ZnO layers are presented in Figure 4. The absorbance of the layers was in visible area, with ZnO layer after CBD and HT treatment band-gap energy (\( E_g \)) value of 3.47 and 3.41 eV, respectively. Our previous research has revealed that \( E_g \) values are very influential on the size of crystallite obtained. The larger the size of the crystallite, the smaller the value of \( E_g \). This corresponds to a shift in the linear region of the curve towards a larger wavelength, this phenomenon is known as red shift [8].

The presence of ethylene around the sensor will reduce its resistance. This phenomenon is influenced by chemical composition, surface modification, surface sensing microstructure and environmental conditions of the sensor (temperature and humidity). The change in the response on exposure to the target gas was calculated using equation [9]
\[
\Delta R (%) = \frac{R_a - R_g}{R_a} \times 100\%
\]  \hspace{1cm} (2)

where \(R_a\) is the resistance before exposure and \(R_g\) is the resistance with the target gas flowing through the chamber. This response change is usually called the response sensitivity; hence the term sensitivity is used here. Besides the sensitivity, we also calculated the response and recovery times, i.e., the time needed for the sensor to reach 90% of its steady-state value [9].

In this study, the ethylene concentration used was 50 ppm, and the sensing performance test was conducted in two different temperature, i.e. 100 and 200ºC. From the calculation, the \(\Delta R\) value can be obtained, and listed in Table 1. The response during ethylene exposure can be seen in Figure 5.
Table 1. The sensors’ response on ethylene gas.

| Sample | Ethylene Concentration (ppm) | Responses (%) |
|--------|------------------------------|---------------|
|        | 50                           | 100°C | 200°C |
| CBD    | 50                           | 1.34  | 2.40  |
| HT     | 50                           | undefined | undefined |

From Table 1, it is noted that the resistance of the ZnO layer in the CBD sample has returned to its original value after the exposure of ethylene gas was stopped. However, this did not occur in the ZnO sample undergoing the HT process. Considering the collapsed structure displayed previously in Figure 2.b., we can assume that damage in the structure may contribute to the sensing performance. Hence, in order to obtain higher response, it is necessary to conduct improvement and sensitizing of the ZnO layer’s surface.

4. Conclusion
In summary, we have developed a ZnO-based sensor for ethylene gas. The as-grown ZnO layer is simple to prepare and has been successfully identified the ethylene gas in concentration of 50 ppm. The sensor response is assumed to be related to the morphology and structure of the ZnO layer on the substrate. From the study, it is revealed that the as-grown ZnO layer has been successfully identified the ethylene gas in concentration of 50 ppm, with response value of 2.40% at 200°C.

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