Growth of zinc oxide nanostructures on glass substrates for ethanol gas sensor application

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Abstract. ZnO nanostructures grown on glass (SiO2) substrates have been successfully fabricated for ethanol gas sensor. These ZnO nanostructures were prepared by chemical bath deposition with various ammonium hydroxide concentrations. The response of ZnO – based ethanol gas sensor exhibited higher response at lower NH4OH concentration; this might be attributed to the uniform morphology of the ZnO nanostructures which facilitates easier interaction with the ethanol gas. On the other hand, at higher NH4OH concentration showed drastic decrease in sensor response. This might be due to the growth of broken nanorods. Scanning electron microscope (SEM) images confirmed the formation of uniform and vertically grown nanostructures with lower concentration of NH4OH. On the other hand, at higher NH4OH concentration, broken nanorods and agglomerations were present as revealed in the SEM micrographs. Energy dispersive x-ray spectroscopy (EDS) measurements suggested that the grown nanostructures were most likely composed of ZnO. The calculated energy band gap from the UV-Vis spectra confirmed that the grown ZnO nanostructures.

1. Introduction
Ethanol (CH3CH2OH) is one of the most significant alcohols with various applications in food industry, brewing process control as well as in the medical and clinical applications. This ethanol is also used as a solvent of various alcohol soluble active ingredients in making perfumes, paints, lacquer and explosives. Furthermore, it is also used as an alternative fuel for automobiles [1]. However, behind these vast applications of ethanol, it also imposes disadvantages. At lower concentrations of ethanol, it can cause behavioural changes or impairment of vision to human [2]. On the other hand, at higher concentration, ethanol is volatile and toxic which causes skin and eye irritation. It may also cause nausea and vomiting when ingested, even death usually occurs if the concentration of ethanol in the bloodstream exceeds about 5%. To prevent such untoward incident, it is really a must for the early detection of ethanol in the environment. One of the best solutions for early detection of ethanol is the use of chemical sensors. Apparently, there are many ethanol sensors that are available in the industry, such as SnO2, WO3, InO3, TiO2 and ZnO. These materials have been extremely used as ethanol sensors due to their excellent sensing properties.

Zinc oxide is a good material for ethanol sensing compared to others because of its feasibility to be used as an ultrahigh sensitive sensors [3], high chemical stability, suitability to doping, non-toxicity, 

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abundance in nature and low cost [4]. These are various techniques that have been applied to synthesize ZnO nanostructures such as metal organic chemical vapour deposition (MOCVD) [5], pulse laser deposition (PLD) [6], molecular beam epitaxy (MBE) [7], radio frequency sputtering and chemical bath deposition. Among these techniques, chemical bath deposition is an attractive method for obtaining the nanostructures and has been extensively employed for the formation of metal oxide thin films and nanostructures which offers large area batch processing deposition and requires only solution containers and substrate mounting devices. Several studies reported that the ZnO nanostructures are very dependent on the NH₄OH concentration being utilized [8,9,14]. There were initial reports that these ZnO nanostructures grown on glass substrates can be fabricated as an ethanol sensor [10-12]. They partially found out that ZnO can be used as a good sensor device. They failed to establish the connection on the effect of utilizing different concentrations of the precursor that could eventually affect the morphology of the grown nanostructures. These morphological changes will have significant effect on the response of the fabricated ZnO-based ethanol gas sensor.

In this work, ZnO nanostructures are synthesized on glass (SiO₂) substrate with different ammonium hydroxide precursors and elucidate its morphological structures. The response of these fabricated ethanol gas sensor will be evaluated.

2. Experimental procedure

The ZnO nanostructures were synthesized on glass (SiO₂) substrates using chemical bath deposition technique. These substrates are thoroughly cleaned with acetone, ethanol and diluted hydrochloric acid to eradicate the impurities present on the substrates. The reagents used were aqueous zinc sulphate (ZnSO₄) and aqueous ammonium hydroxide (NH₄OH) solution. The concentration used for ZnSO₄ was maintained constant at 0.03 M while for NH₄OH concentration, it was varied to 1.0 M and 3.0 M concentrations. In these concentrations, the resulting ZnO nanostructures adhered well on amorphous glass substrates. The surface morphology and elemental composition of the grown nanostructures were characterized using scanning electron microscopy – energy dispersive x-ray spectroscopy (SEM-EDS), respectively. Optical reflectance was carried out in the wavelength 200-1000 nm by using ultraviolet-visible (UV-Vis) spectroscopy. Two-point probe method was also utilized to obtain the electrical characteristics of the synthesized ZnO nanostructures. Figure 1 depicts the sensor configuration while Figure 2 shows the schematic diagram for the two-probe method.

Figure 1. The sensor configuration where in (1) copper wires as the electrodes, (2) silver paste, (3) SiO₂ substrate and (4) microscopic glass slide.

Figure 2. Schematic diagram of two-point probe method.
3. Results and discussion

3.1. Response of ZnO-based sensor device to ethanol gas

Figure 3 shows the response on ethanol gas of ZnO-based sensor using glass substrate prepared from 0.03M ZnSO₄ and different NH₄OH (1.0 M and 3.0 M) concentrations. It can be observed that the ZnO nanostructures deposited on glass substrate with 1.0 M NH₄OH responded to the ethanol gas and it has the higher sensitivity of about 33.75%. This high response to ethanol gas might be attributed to the uniformity of the nanorods. The uniformity of the grown nanostructures exhibit higher response due to higher surface area being exposed to ethanol gas. On the other hand, at 3.0 M NH₄OH revealed a lower sensitivity of about 4.21%. This might due to the morphology of the nanostructures as revealed in Fig. 5 (b). It can be further observed that the 1.0 M NH₄OH concentration was not able to recover to its original state after exposure to ethanol gas.

![Figure 3](image)

**Figure 3.** The response of the ZnO-based sensor under ethanol environment with 1.0 M and 3.0 M NH₄OH concentrations.

3.2. I-V curve of the ZnO-based sensor

The current-voltage (I-V) characteristics of the ZnO-based sensors were measured to determine the recovery of the fabricated sensor after exposure to ethanol gas. It is believed that when a sensor is fully recovered to its original state, the I-V curve has no changes before and after exposure to ethanol gas. It can be seen in Figure 4 (a) that the I-V characteristics of ZnO/SiO₂ with 1.0 M NH₄OH concentration exhibit a drastic decreased on the resistances of about 17.45%, before and after exposure to ethanol gas. This indicates that the ZnO-based sensor was not able to return to its original state. The same observation occurs at 3.0 M NH₄OH concentration as shown in Figure 4 (b).

![Figure 4](image)

**Figure 4.** The I-V characteristics of ZnO/SiO₂ prepared using (a) 1.0 M and (b) 3.0 M NH₄OH concentrations.
3.3. **Surface morphology of the grown ZnO nanostructures**

In Figure 5 showed the surface morphology of ZnO nanostructures prepared at 1.0 M NH$_4$OH and 3.0 M NH$_4$OH concentrations. The 1.0 M NH$_4$OH concentration exhibits uniform nanorods. However, at higher NH$_4$OH concentration of about 3.0 M, agglomerations and broken nanorods can be observed. This phenomenon might be due to the higher concentration of OH$^-$ ions that may trigger dissolution and etching [9,16].

![Figure 5](image)

**Figure 5.** SEM images for ZnO deposited on glass substrates prepared with (a) 1.0 M and (b) 3.0 M NH$_4$OH concentrations.

3.4. **Energy band gap**

The optical band gaps of ZnO nanostructures were obtained through the use of the UV-Vis reflectance spectra [15]. Figure 6 depicts the extrapolated optical band gap of the samples prepared with 1.0 M and 3.0 M NH$_4$OH concentrations. Through linear fitting the extrapolated band gap for 1.0 M NH$_4$OH is 3.34 eV while the energy band gap of 3.0 M NH$_4$OH concentration gives 3.28 eV. These values were in good agreement to the reported band gap energy of ZnO [13].

![Figure 6](image)

**Figure 6.** Variation of $h\nu (\ln(R_{\text{max}}-R_{\text{min}})/(R-R_{\text{min}}))$ vs ($h\nu$) of the fabricated ZnO samples grown at (a) 1.0 M and (b) 3.0 M NH$_4$OH concentrations.

4. **Summary**

The response of ZnO nanostructures to ethanol gas was successfully investigated. It shows that 1.0 M NH$_4$OH concentration exhibits higher response as compared to 3.0 M NH$_4$OH. It has been observed that this response might be due to the uniform morphology of the samples as revealed it the SEM micrographs. It was shown that the sensitivity of ZnO nanostructures grown on glass substrates prepared from 1.0 M NH$_4$OH concentration exhibits the highest sensitivity due to the uniformity of
ZnO nanostructures grown on the substrate surface. At higher concentration of NH₄OH, there was a small response of fabricated ZnO nanostructures sensor as exposed to ethanol gas. SEM micrographs revealed a non-uniform growth of the nanorods, instead agglomerations and broken nanorods were found. The fabricated ZnO – based sensor with lower concentrations of NH₄OH showed the highest response to ethanol gas. In contrast, the fabricated ZnO – based sensor with higher concentration of NH₄OH showed a low response to ethanol gas. The calculated energy band gap of ZnO nanostructure is in good agreement to the reported value.

5. References

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Acknowledgment

K Emphasis would like to acknowledge the Commission on Higher Education (CHED) for the scholarship grant. We would like to thank Philippine Council for Industry, Energy and Emerging Technology Research and Development – Department of Science and Technology (PCIEERD-DOST) for the laboratory equipment.