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Fabrication of Zinc Oxide Nanostructured Based Gas Sensor

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Abstract: Zinc Oxide (ZnO) is a metal oxide semiconductor material that has been extensively studied and one of the promising materials for gas detection application. Compared to bulk materials, nanostructures with higher surface-to-volume ratio able to improve the performance of material in gas detection. In this study, ZnO nanorods and nanoflowers were synthesized by hydrothermal method, and their morphology-dependent gas sensing properties were investigated. Field Emission Scanning Electron Microscopy (FESEM) was used to confirm the properties of these two types of nanostructures. ZnO nanorods growth in alkaline solution have distinctively longer length nanorods clusters with hexagonally shaped tips. A cluster of short nanorods formed in the neutral solution. Although both morphologies have shown good sensitivity towards ethanol, the response of nanoflowers was higher than that of nanorods which was attributed to its relatively higher surface area and amount of surface defects. Furthermore, the electrode arrangement dependent gas sensing properties were investigated. The nanorods with interdigitated electrode have good sensitivity when deal with ethanol. Closely packed electrode of interdigitated has successfully enhanced the sensitivity of the device.

Keywords: ZnO, Nanostructure, Hydrothermal, Gas sensor, Sensitivity

1. Introduction

Gas sensors act as one of the most crucial pieces of equipment for detecting hazardous gases, monitoring gas concentration, and environmental data to ensure industrial safety [1]. However, metal oxide semiconductors (MOS) are frequently the first choice for manufacturing gas sensors due to their

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simplicity of manufacture, excellent sensitivity, stability, and low cost [2]. ZnO-based sensors have gotten much attention from people all around the world. In comparison to other compound semiconductors, ZnO has a substantial exciton binding energy (60 meV) and sizeable direct bandgap (3.37 eV) as well as ease of manufacture [3]. It is one of the essential materials for producing low-cost sensors since it has a high response rate to chemical poison gases and excellent selectivity and sensitivity [4]. The gas sensing characteristics and material properties, such as size and morphology, are dependent on the specific synthesis process [5]. However, due to the advantages of simple equipment, low cost, and mild preparation conditions, the easiest way to manufacture will generally be chosen, such as the hydrothermal method. The planar device structure is always employed to fabricate ZnO-based gas sensor devices due to its straightforward design and production method with significant cost savings [6]. However, interdigitated electrodes (IDEs) have been introduced to boost the sensitivity of gas sensors since they allow for a more excellent contact surface between the electrodes within a compact region [7].

ZnO nanostructures have become the most appealing candidates for manufacturing ZnO gas sensing devices, but a study should be conducted to identify this statement. First, it is essential to systematically study the ZnO nanostructures fabrication process to synthesize different nanostructures. Different morphology of ZnO nanostructures will contribute to the different performance of gas sensors, but with a promising nanostructure, a gas sensor with high sensitivity will be obtained. Furthermore, different arrangements for the electrode in a gas sensor may affect the performance of the gas sensor. Hence, the sensitivity of gas sensor for both parallel contact electrodes and interdigitated electrodes should also be studied.

2. Materials and Methods

2.1 Materials Specifications

The required analytical chemical to form ZnO nanostructrues used zinc acetate dihydrate, [$Zn(CH_3CO_2)_2 \cdot 2H_2O$], and hexamethylenetetramine (HMTA), [$C_6H_{12}N_4$]. In this experiment, zinc acetate dihydrate was used as a precursor to generating ZnO nanostructures and HMTA act as a pH regulator in generating the hydroxide ion [8]. Ethanol is used to form the gas to study the ethanol gas-sensing properties of ZnO nanostructures.

2.2 Methods

ZnO solution were prepared by hydrothermal method. Zinc acetate dihydrate, [$Zn(CH_3CO_2)_2 \cdot 2H_2O$], and hexamethylenetetramine (HMTA), [$C_6H_{12}N_4$] were the two materials that used for the synthesis of ZnO nanorods and nanoflowers. 25 mmol of both of the materials were weighted and dissolved in 50 mL of deionized (DI) water place the stirrer inside the beaker and stirred the solution for 1 hour at 300 rpm.

Then immersed the substrate in the beaker and place inside the hot air oven at 90 °C constant temperature for 4.5 hours. After 4.5 hours, take out the substrate and rinsed and dried at 110 °C for 30 minutes. To prepared a metal contact on the substrate, gold (Au) was deposited by using DC sputter coater. Finally, place the substrate in a homemade gas testing setup located on the hot plate with the temperature of 250 °C, and insert the ethanol. The readings obtained from the electrometer of resistance changes over time were recorded. The data collected were plotted by using OriginLab to investigates the properties of the samples when deal with ethanol gas.

2.3 Characterization

Surface morphologies of ZnO nanorods and nanoflowers were examined by FESEM, and gas sensing properties of ZnO were carried out using a DIY gas testing equipment and an electrometer.

2.4 Formulae

Sensitivity can be defined as the percentage change in the resistance of the samples in the presence and absence of gas.

$$S = \frac{R_{gas} - R_{air}}{R_{air}} \times 100\% \qquad \text{Eq. 1}$$

S represents sensitivity, R_{gas} is denote the resistance in ethanol gas and R_{air} represents the resistance in dry air.

3. Results and Discussion

3.1 Results

Figure 1 and 2 represented the FESEM images of hydrothermally grown ZnO nanorods and nanoflowers formed. Figure 1(a) and Figure 2(a) represents the low magnification FESEM images (x1000), while the Figure 1(b) and Figure 2(b) images show the high magnification FESEM images (x5000). In low magnification images, the growth region, compatibility and the growth alignment of nanostructures can be successfully observed. However, the high magnification images focus on the growth pattern and size of the nanostructure formed.

From Figure 1, it be can observed that the hexagonal ZnO nanorods clusters were formed with thicker rods in the middle. The thick rods have measures in diameter of about 3.182 µm. Surrounding the thicker rods, are smaller nanorods measuring about 1.227 µm. It formed homocentric nanoflower in which a nucleation centre is emerged at the centre of a nanorod [9]. The overgrowth is due to the high concentration of chemicals and time of growth. The high concentration leads to larger clusters and yet shorter length of nanorods.

On the other hand, Figure 2 shows that the nanostructures have distinctively longer length nanorods clusters with hexagonally shaped tips. If compared with sample growth in low pH, sample growth in pH 11 with bundled longer nanorods of length about 6.712 µm. A cluster of short nanorods with a length about 4.911 µm formed in the neutral solution. More tetraamminezinc (II) ions are easily converted to ZnO in the function of weak hydroxide ions when the concentration of ammonia in the system is low. Thus, several ZnO nuclei are generated early on, providing a possibility for the development of shorter bundles of nanorods. When ammonia concentrations are high, the hydroxide ion has a higher quality, which is advantageous for tetraamminezinc (II) ion in the formation of ZnO nuclei. Therefore, in the sample with high pH value, there are few single and more bungled nanorods formed. Additionally, a high quality of zinc hydroxide ion at high pH slows down the speed of ZnO crystalline formation, which, after a prolonged reaction time, produces enough ZnO nuclei produced by the zinc hydroxide ion [10]. Long and uniform rods formed in pH 11 shows the characteristic form ZnO nanoflowers.

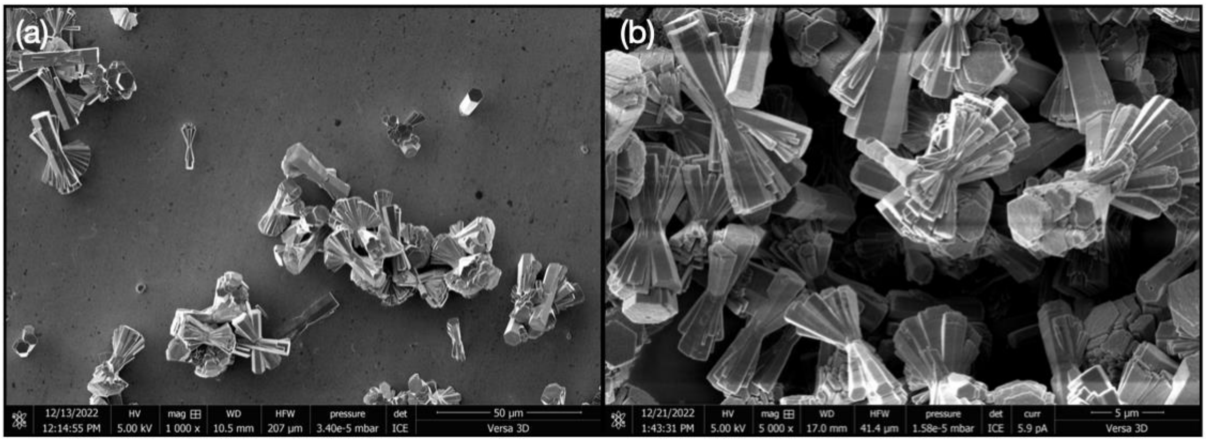

Figure 1: FESEM image of ZnO growth at pH 6.61

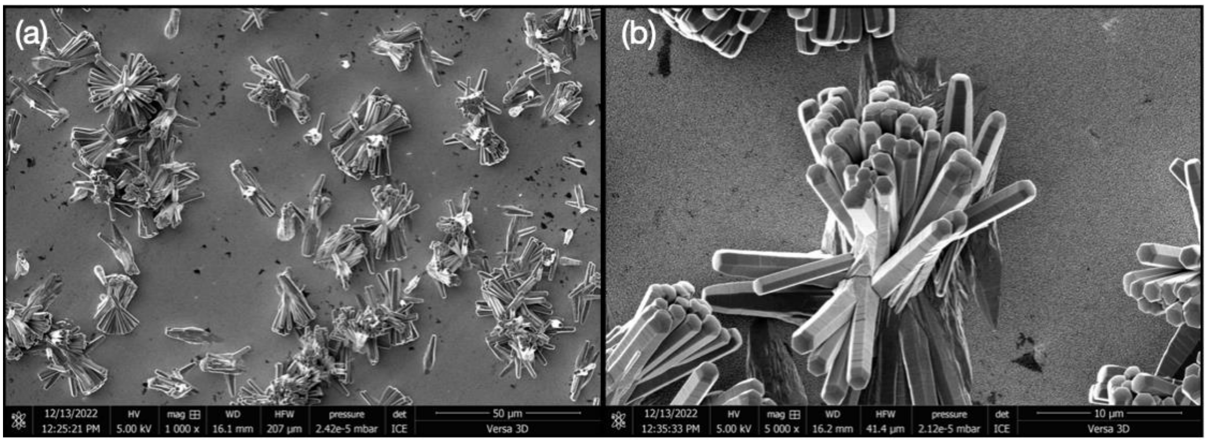

Figure 2: FESEM image of ZnO growth at pH 11

3.2 Ethanol gas sensing properties for ZnO nanostructure with different electrode arrangement

Figure 3 shows the properties of ZnO nanorods in gas sensing when deposited different arrangements of metal contact. Figure 3(a) represents the ZnO nanorods deposited with the parallel electrode, S1, while Figure 3(b) represents the ZnO nanorods deposited with an interdigitated electrode, S2.

The initial resistance shown in Figure 3 experienced some non-consistent increases and decreases. These are because the O^- ions produced during the process have fully covered and attached to the surface of ZnO nanorods. At the same time, the free electron is still freely transferred and experiences collision with each other. ZnO nanorods showed a very unstable response towards ethanol vapour, resulting in a low number of electron transfers and low change in resistance recorded for the early exposure stage.

The lowest resistance can be explained as the most substantial interaction between ZnO and the molecule in ethanol. In the comparison of Figures 3(a) and Figure 3(b), the resistance difference between the peak and trough experienced by S1 is 1.5 Ω, while for S2 is 4.8 Ω. According to Eq.1, the sensitivity of S1 is 11.28% while for S2 is 23.76%. So, the ZnO nanorods with interdigitated electrodes experienced a better sensitivity when dealing with ethanol gas. Due to the near proximity of the cathodic and anodic electrodes, small quantities of ionic species can easily cycle across the electrode, providing an advantage in the detection of a small amount of analyte and enhancing sensitivity performance [11]. As a result, a more precise and capable sensor has emerged.

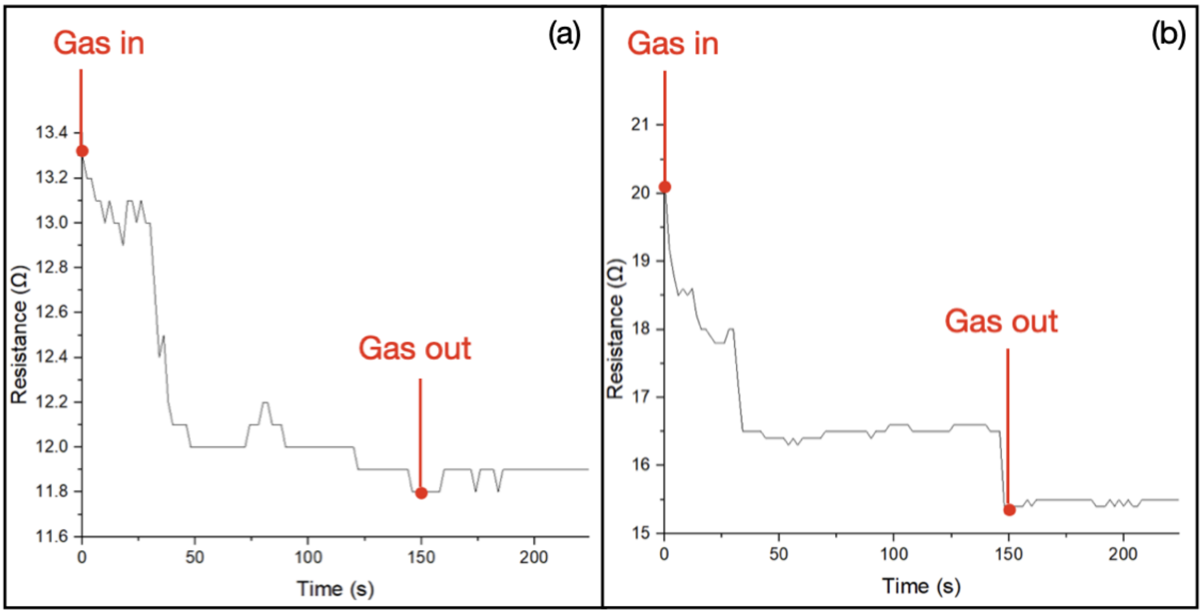

Figure 3: ZnO nanorods with (a) parallel, S1 (b) interdigitated electrode, S2

3.3 Ethanol gas sensing properties for ZnO nanostructure with different morphologies

Figure 4 shows the properties of different ZnO morphologies in gas sensing when deals with ethanol gas, Figure 4(a) represents the ZnO nanorods, S1 while Figure 4(b) represents the ZnO nanoflowers, S3.

According to Figure 4, ZnO nanoflowers displayed the highest responsiveness to ethanol than nanorods at the same temperature (250 °C). The nanoflowers device experienced a rapid and significant resistance dropped to its lowest resistance value within 15 s. However, the nanorods device dropped the resistance to its lowest value by using the time of approximately 150 s. Apart from that, the resistance dropped of nanoflowers is much higher than the resistance dropped of nanorods.

In the comparison of Figures 4(a) and Figure 4(b), the resistance difference between the peak and trough experienced by S1 is 1.5 Ω, while for S3 is 2.5 Ω. According to Eq.1, the sensitivity of S1 is 11.28% while for S3 is 14.04%. So, the ZnO nanoflowers experienced a better sensitivity when dealing with ethanol gas. The difference could be ascribed to the two nanomaterials' distinctly different morphologies, where the nanoflowers may have more surface flaws and surface area than nanorods, which allowed the ethanol molecule to be better adsorbed [12]. It deals with higher detection and the interaction between ethanol vapour and ZnO nanoflowers. The increases of resistance in the end of the process in Figure 4 shows the nanoflowers device begin with the process to recover to the original baseline response when the gas is removed. This can conclude that ZnO nanoflowers has higher sensitivity and recovery rate compared with ZnO nanorods.

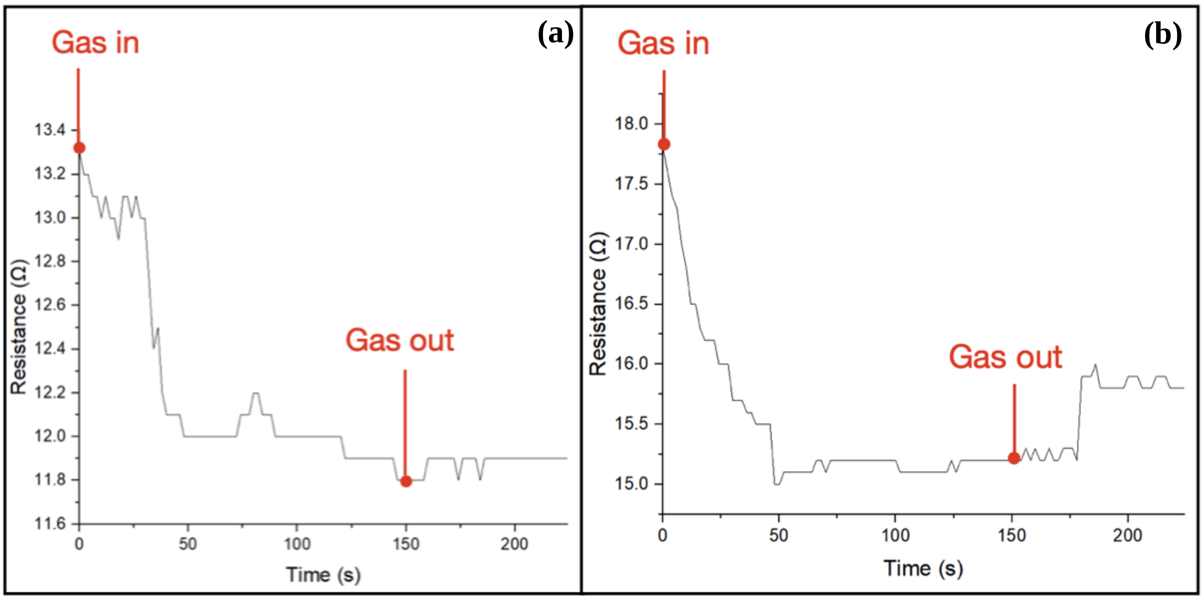

Figure 4: (a) ZnO nanorods, S1 (b) ZnO nanoflowers, S3

4. Conclusion

In conclusion, ZnO nanorods and nanoflowers were fabricated using a low-cost hydrothermal approach. FESEM images indicate that when the pH value rises, the length of nanostructures grows along with it. The sensitivity of the samples can be determined by the percentage change in the resistance of the samples in the presence and absence of gas. In comparison of two morphologies, ZnO nanoflowers has higher sensitivity and recovery rate compared with ZnO nanorods. These situations happened because nanoflowers with higher surface area and surface defects would enhance the adsorption of ethanol molecules and increase the detection ability. However, for the sample with interdigitated electrode has good sensitivity compared to parallel electrode due to a closely packed electrode, which easy for ion to be transferred.

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