Chemical Bath Deposited ZnO Nanowires for H_2 Gas Sensors: Optimisation of Deposition Time

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Abstract - The metal oxide semiconductor-based gas sensors play a vital role in detecting toxic, explosive and combustible gases in the environment. ZnO is an n-type metal oxide used as a promising material in gas sensing applications. Recently, ZnO-based one-dimensional nanowires have been taken much attention in gas sensors due to their high surface-to-volume ratio. In this study, ZnO nanowires were grown through chemical bath deposition (CBD) at different deposition times (2, 4, 6 and 8 h) and investigated the response change of the gas sensors towards H_2 gas at 100 °C. ZnO nanowires were grown on a borosilicate glass substrate pretreated with a seed layer. The seed layer was deposited using the Jet Nebulizer Spray Pyrolysis (JNSP) method. ZnO nanowires were grown using $Zn(NO_3)_2$ and hexamethylene tetraamine (HMTA) during the CBD process. The obtained nanowires at different deposition times were investigated for their structural (XRD), morphological (SEM), and optical (UV-Visible spectroscopy) properties. According to the SEM analysis, the nanowires grown for 6 hours had the highest aspect ratio of 30, with a diameter of 90 nm and the highest length of 3 µm. XRD analysis revealed that the synthesized hexagonal ZnO nanowires were preferentially oriented in the (002) plane. Deposited nanowires were later used to fabricate H_2-sensitive gas sensors. Gas sensing results showed the highest response change of 9.36 to 100 ppm H_2 at 100 °C for the nanowires grown for 6 hours. Obtained results concluded that the optimum ZnO nanowires deposition time is 6 hours for the deposition method used.

Keywords: Chemical bath deposition, Deposition time, Gas sensors, Spray-coated seed layer, ZnO nanowires

I. INTRODUCTION

Numerous factors have been the source of the releasing of a vast amount of toxic, explosive, and flammable gases to the environment. Therefore, it is essential to identify toxic gases like H_2S, NH_3, CO, H_2, and LPG to safeguard humankind. Hence, scientists have been working on various types of gas sensors to detect mentioned chemical gases. Among these types, metal oxide (MOx) semiconductor-based gas sensors stand out due to their high sensitivity, fast recovery, low working temperature, and low cost. ZnO and SnO_2 are the most studied martials so far as MOx gas sensors, and further investigations are been carried out to inent superior gas sensing devices. The sensitivity of the gas sensor enhances by the nano-sized MOx by increasing the surface-to-volume ratio. This research thoroughly focused on synthesising ZnO nanowire-based gas sensor through the chemical bath deposition (CBD) technique, which is one of the most scalable, low-cost wet chemical techniques. Special attention was paid to optimize the CBD deposition time of the ZnO nanowires to fabricate highly sensitive H_2 gas sensors.

II. MATERIALS AND METHOD

Firstly, borosilicate substrates were cut into 2.5 cm × 2.0 cm pieces and thoroughly cleaned with detergent. Then, they were washed with DI water and dried. Then substrates were sonicated in dilute HCl solution, and the previous step was repeated. Then, the glass plates were cleaned by immersing in the order of acetone, methanol, and isopropanol just below their respective boiling points. Chemically cleaned substrates were then washed with DI water and dried with Nitrogen before being stored in a desiccator. The substrates were plasma cleaned for 5 minutes to obtain a better hydrophilic surface.

ZnO seed solution was prepared with 0.1 M solutions of Zinc acetate dehydrate [$Zn(CH_3COO)_2.2H_2O$ – 99.5%] with monoethanolamine (MEA) [$NH_2CH_2CH_2OH$] [1]. The molar ratio between zinc acetate and MEA was 1. The solution was sonicated for 15 minutes and stirred for 2 hours at 300 rpm and 70 °C. The resulting milky solution was aged for 24 hours at room temperature. The solution was then spray-coated on the cleaned glass substrate 10 times. Throughout the process, the substrate was placed on a hot plate at 120 °C.

ZnO NWs were grown with an equimolar (0.1 M) aqueous solution of zinc nitrate hexahydrate [$Zn(NO_3)_2.6H_2O$ – 99.5%] and hexamethylenetetramine [$C_6H_{12}N_4$ – 99.5%]. The prepared substrates with seed layers were used for CBD at 90 °C and a rate of 700 rpm. The deposition time was varied as2 h, 4 h, 6 h, and 8 h. After the CBD process, samples were rinsed with DI water and dried in air. Finally, the samples were annealed in air at 300 °C for half an hour.

III. RESULTS AND DISCUSSION

A. *Morphological characterization*

The ZnO nanowires were grown at different deposition times. The deposited nanowires were morphologically analysed using FESEM imaging. The length, morphology, diameter, and surface density of nanowires were examined.

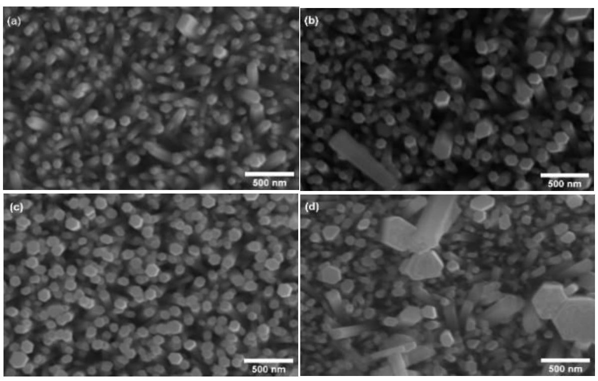

Fig. 1. The FESEM images of ZnO nanowires grown for (a) 2 h (b) 4 h (c) 6 h and (d) 8 h

Fig. 1 illustrates the FESEM images of nanowires grown seeded borosilicate substrates at different CBD deposition times. Nanowire diameter and lengths were measured using ImageJ software. The diameter of the NWs increased from 70-150 nm with the deposition time [1]. But the length of the nanowires increased up to the nanowires grown for 6 h. Nanowires grown for 8 h possess the highest diameter and the lowest length of 740 nm. According to the Fig. 1 (d) image, the diameter of the nanowires increased due to the coalescence of smaller nanowires with nearby nanowires and formed the outer ZnO layer. The length of the nanowires was fallen due to the pH of the medium. CBD process governs the HMTA concentration, which creates OH^- ions in the medium. With time, the OH^- concentration of the medium began to decrease. After that, two factors become dominant. One is the pH of the medium is reduced. In the low pH conditions, which create extreme acidic mediums, it is hard to form ZnO due to the dissolution of ZnO [2]. Besides that, due to the lack of OH^- in the solution, the ZnO forming reaction rate becomes slower. Therefore, the length of the nanowires is reduced with time. Therefore, according to the results, the length reduction after 6 h may be due to the above facts.

Also, the density of NWs per unit area increases as the deposition time increases to 6 h. Nanowires deposited for 8 h has the lowest surface density of 60 μm^{-1}. As seen in the SEM images, with the increment of the time duration of the deposition vertical alignment of the nanowires increases [1]. Even though the nanowires grown for 2 h have the lowest diameter, they are poor in vertical orientation compared to the Fig. 1 (c). Therefore, the surface density is lower than nanowires grown for 6 h.

B. H_2 gas sensing results

In this study sensing response of the prepared gas sensors was investigated using 100 ppm H_2 gas at the operating temperature of 100 °C. Fig. 2 shows the sensing response of the sensors fabricated by varying the deposition time of the ZnO nanowire.

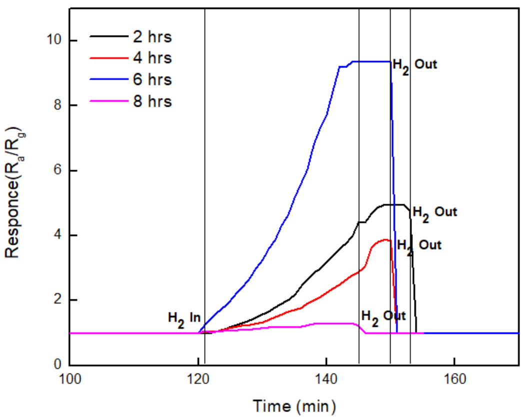

Fig. 2. Response change of the ZnO nanowire sensors grown for different deposition times when exposed to H2 with concentration levels of 100 ppm at 100 °C

It was observed that the deposition time dramatically influences the gas sensing property of the sensor since it enhances the NW density of the sensor. As shown in Fig. 2, the response of the sensor increased with increasing seed layer thickness and obtained the highest response for NWs grown for 6 h at 100 °C. That is maybe because the surface density of the NWs influenced by the increasing deposition time. With the increase of NW density, the reaction sites of the sensor increase [3]. Since gas sensing is a surface reaction, the sensor response increases with the number of reaction sites. Therefore, with the increment of surface density, the response of the sensors towards H_2 gas increased.

IV. Conclusion

To summarize, Nanowires of ZnO semiconductor MOx can be effectively synthesize through the chemical bath deposition method. Deposited ZnO nanowires can be used to fabricate highly sensitive H_2 gas sensors. The CBD deposition time has a significant impact on the morphology as well as the gas sensing behaviour of the ZnO nanowires. The seed layer was deposited using JNSP method. Nanowires grown for 6 h have the highest aspect ratio and are properly vertical oriented. Also, it has the highest surface density, which is an essential factor as a gas sensor. It has shown the highest response change to H_2 gas compared with the nanowires grown for 2 h, 4 h, and 8 h.

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Reference

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