Chemical bath deposition growth and characterization of zinc oxide nanostructures on plain and platinum-coated glass substrates for hydrogen peroxide gas sensor application

Y D J Jamasali¹ and A C Alguno
Physics Department, Mindanao State University–Iligan Institute of Technology, A. Bonifacio Avenue, Iligan City 9200, Philippines

Email: yusofdenj@gmail.com, alphaarnie@yahoo.com

Abstract. Growth of zinc oxide on plain and Pt-coated glass substrate via chemical bath deposition technique (CBD) were studied. Aqueous solutions of ammonium hydroxide (NH₄OH) and zinc sulfate (ZnSO₄) were used as the precursor substances in the synthesis. Ultraviolet-visible spectroscopy (UV-Vis) was performed to determine the energy band gap and X-ray diffraction (XRD) to examine crystallinity. Sensitivity measurements were carried out in order to examine its potential to be fabricated as hydrogen peroxide (H₂O₂) gas sensor. Experimental results in the sensitivity experiment show that in the presence of H₂O₂ gas, the resistance of ZnO increase which can be used as the basis for H₂O₂ detection. UV-Vis showed variation of energy band gap values but were all near the generally accepted value. XRD spectra further verify that ZnO were indeed synthesized.

1. Introduction
The large varieties of applications of hydrogen peroxide (H₂O₂) have continued to increase over the last decades. Its vapor can act as sterilant in the food industry [1,2]. Its liquid compound is used in hair bleaching and hair dyes [3] and medically important as antiseptic and disinfectant [4]. Nevertheless, H₂O₂ can be harmful in concentrations higher than 35%. It is an aggressive oxidizer and can pose several risks including explosive vapors, hazardous reactions, corrosive internal ailment, and skin disorder [5]. Over the past 15 years, three bleach plants in North America experienced catastrophic events caused by decomposition of H₂O₂ which resulted in serious injuries [6]. Also, disastrous events like the sinking of the Russian Kursk submarine in 2000 [7], and explosions in wastewater treatment tanks [8] have occurred due to H₂O₂ reactions.

To reduce risks, several researches were directed on the early detection of H₂O₂ gas. Recently, there has been a number of studies in order to fabricate H₂O₂ gas sensors employing several routes in detecting H₂O₂ such as sensors based on thermocouple [9], gold (Au) and platinum (Pt) electrodes [10], and Prussian – blue [11]. However, these materials are expensive and its processing technique is difficult to perform and required high vacuum technology. Therefore, it is imperative to find an alternative material that offers promising properties that can detect H₂O₂ gas. A good candidate as an alternative material is the semiconductor zinc oxide (ZnO) because it has strong surface sensitivity [12]. It is naturally grown n-type II-VI semiconductor. It has direct band gap of 3.37 eV at room temperature and has a large exciton binding energy of 60 meV which is necessarily adequate to overcome the thermal energy at room temperature [13].

¹ To whom any correspondence should be addressed.
There are various techniques to synthesize ZnO such as metal organic chemical vapor deposition (MOCVD) [14], molecular beam epitaxy (MBE) [15], pulse laser deposition (PLD) [16,17], and chemical vapor deposition (CVD) [18]. But these techniques are very expensive, highly toxic, high cost in environmental disposal and they need high vacuum equipment. Nonetheless, it is essential to find another technique to grow ZnO that offers low cost and does not need high vacuum equipment.

Nowadays, it is believed that chemical bath deposition (CBD) technique might be the cheapest method to deposit ZnO nanostructures. It does not require sophisticated instruments while the starting chemicals are commonly available and cheap, and the preparation parameters are easily controlled [19]. And this technique does not need high vacuum equipment.

Basically, CBD can be classified into two: unseeded and seeded processes. In unseeded, the CBD grows the nanostructures after the substrates had undergone conventional washing [20]. In seeded, before the CBD growing of nanostructures, substrates are pre–treated after conventional washing in order to create seed layers of ZnO [21].

ZnO has also been fabricated as sensor to detect various species. This includes fabricating ZnO as methane sensor [22], LPG sensor [23], ultraviolet radiation sensor [24], and calcium ion sensor [25]. But to the best of our knowledge, there has been no report that ZnO nanostructures synthesized via CBD have been utilized as H$_2$O$_2$ sensor. In this study, ZnO nanostructures are grown on plain and Platinum (Pt) coated glass substrates and then fabricated as H$_2$O$_2$ gas sensors. Sensitivity to H$_2$O$_2$ gas of the fabricated ZnO–based sensors was measured. Energy band gap determinations were carried out via UV-Vis spectroscopy.

2. Procedure

2.1. Cleaning of glass substrate

The very first step before the CBD proper is the washing of glass substrate in order to remove dirt and impurities that may have unknowingly settled on the glass substrate. This is done by washing in several substances, namely: acetone, distilled water, ethanol, distilled water again, hydrochloric acid (HCl), and lastly distilled water. These glass substrates are then dried in air at room temperature.

2.2. Platinum coating

After the glass substrates are dried, some of these were coated with platinum using a platinum auto-coater machine shown in Figure 1.

In coating a cleaned glass substrate, platinum auto-coater machine is used with pressure 4 Pa and 40 A current. The glass substrate is placed at the center-stage of the machine and the area is vacuumed for 10 seconds. The machine coated the substrate with platinum through spray sputtering for 60 s.

2.3. Seeded (two-stage) CBD

The seeded (two–stage) CBD commence with the making of Ammonium zincate bath solution which is done by combining 100 mL of 0.03 M ZnSO$_4$ and 100 mL of 1 M NH$_4$OH (in another trial this is 3 M) in a 250–mL beaker. This beaker is placed inside a 1000–mL beaker with water having the same level as the solution inside the 250–mL beaker. The bath is stirred at a constant rate of 360 RPM by magnetic stirrer for 30 minutes and its temperature is not varied, the same with room temperature. The solution was then maintained at 70°C and stirred at a constant rate of 360 RPM for 5 hours. The outcome of this were white precipitates, which were most likely ZnO settled at the bottom and some on the walls of the beaker. These precipitates are carefully scooped and then placed on the cleaned plain and Pt-coated glass substrates. They are then oven-dried at temperature 200°C. These are now the seeded substrates.

Afterwards, another Ammonium zincate bath solution is made, and stirred, as mentioned above. Then, the seeded substrates were lowered and submerged in the bath. The solution was heated and maintained at 70°C and stirred at a constant rate of 360 RPM for 5 hours (refer to Figure 2).
Figure 1. Platinum coating. (a) The center stage, opened and the cleaned glass substrates were placed inside. (b) Pt-coating on process. The number on the display shows the countdown time (in s).

Figure 2. Essential constituents in chemical bath deposition (CBD) of zinc oxide (ZnO).

3. Chemical reactions involved

The ammonium zincate bath undergoes chemical reaction between ammonium hydroxide and an aqueous solution of zinc sulfate (ZnSO₄):

$$\text{ZnSO}_4 + 2\text{NH}_4\text{OH}_{(aq)} \rightarrow \text{Zn(OH)}_{2(s)} + (\text{NH}_4)_2\text{SO}_4 \quad (1)$$

Addition of ammonia dissolves the precipitate following the reaction.

$$\text{Zn(OH)}_{2(s)} + 2\text{NH}_4\text{OH}_{(aq)} \rightarrow (\text{NH}_4)_2\text{ZnO}_2 + 2\text{H}_2\text{O} \quad (2)$$

The overall reaction:

$$\text{ZnSO}_4 + 4\text{NH}_4\text{OH}_{(aq)} \rightarrow (\text{NH}_4)_2\text{ZnO}_2_{(s)} + (\text{NH}_4)_2\text{SO}_4 + 2\text{H}_2\text{O} \quad (3)$$

And the reaction occurring on the surface of the substrate leading to the formation of ZnO from ammonium zincate bath is [20]:

$$\text{(NH}_4)_2\text{ZnO}_2_{(s)} + \text{H}_2\text{O}_{(g)} \rightarrow \text{ZnO}_{(s)} + 2\text{NH}_4\text{OH}_{(aq)} \quad (4)$$
4. Characterizations

4.1. Sensitivity measurement
Small portions with dimension of about 1 mm × 1 mm of the synthesized ZnO samples were cut and were fabricated as H$_2$O$_2$ gas sensor by connecting to it thin wires (refer to figure 3) and were put into a circuit (refer to figure 4) to monitor the current and voltage in the absence and presence of H$_2$O$_2$ gas.

In measuring the sensitivity the current pumped by the low current source is held to a fixed value. And the sensitivity is calculated by using the following formula [26]:

$$\text{Sensitivity} = \frac{R_s - R_o}{R_o} \times 100 \% \quad (5)$$

where $R_o$ and $R_s$ are the resistances of ZnO sample before and during/after exposure to H$_2$O$_2$ gas.

The IV curve measurement uses the same circuit used in sensitivity measurement. The only difference is that here, the current was continuously varied and the corresponding voltage was monitored before, during and after exposure to

![Figure 3. Schematic diagram of the ZnO sample fabricated as H$_2$O$_2$ gas sensor.](image)

4.2. UV-Vis spectra
The UV-Vis spectra were obtained Perkin Elmer Lambda 35 UV/Vis Spectrometer.

4.3. XRD
The structural properties were studied by X-ray Diffraction measurements (XRD) with CuK$_{\alpha}$ radiation.

The XRD spectra were obtained from National Institute of Geological Sciences (NIGS) of University of the Philippines.

5. Results and discussion

5.1. Sensitivity and IV curve
Both the uncoated and Pt-coated ZnO samples were fabricated as H$_2$O$_2$ sensors according to the description shown in figure 3.

While ZnO sample was connected to the circuit described by figure 4, current and voltage were measured and the resistance was calculated during every 5 min with and without the presence of H$_2$O$_2$ gas. Figure 5 shows the sensitivity graph of the sample. Clearly, the sensitivity value does not considerably change when the sample was not yet exposed to H$_2$O$_2$ gas. However, once the H$_2$O$_2$ gas is injected to the vicinity of ZnO sample, the sensitivity value increases abruptly. And this continues to increase as time goes on. But when the source of H$_2$O$_2$ gas is shut off, the sensitivity value suddenly decreases to a lower value and approximately maintains that value.

The increase in the sensitivity value during the exposure may have been caused by the increase in the number of oxygen ions occupying the surface ZnO. These ions are the outcome of adsorption of oxygen gas molecules. This oxygen gas comes from the following chemical decomposition of H$_2$O$_2$ which happens when it is exposed to heat, light, sunlight or comes into contact with a metallic surface:

$$\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad \text{(6)}$$

Some electrons, instead of participating in the electron-hole recombination, are trapped by these oxygen ions (as illustrated in Fig. 6) [26]. Hence, increase in the number of oxygen on the surface of ZnO may trigger the increase in resistance of the ZnO sample as a whole and thus, the increase in sensitivity value according to Eq. 5.

![Figure 5. Sensitivity measurement of the ZnO sample.](image)

The samples grown from the bath containing 1 M NH$_4$OH have greater capability of detecting H$_2$O$_2$ gas than those from 3 M NH$_4$OH. And ZnO grown on Pt-coated substrates have less capability of detecting H$_2$O$_2$ gas than those grown on plain substrate. The annealed samples have less responsivity than their unannealed counterparts (as grown) but they have more ability to recover.

![Figure 6. Schematic sketch of the ZnO film’s surface with Oxygen gas becoming Oxygen anion by trapping electrons][26].

5.2. UV-Vis
The $\alpha(h\nu)^2$ versus $h\nu$ graph of all the annealed samples is shown in Figure 7. These curves are based
on the UV-Vis reflectance spectra. Through linear fitting, the extrapolated energy band gap of the samples on plain glass substrates are 3.32 eV and 3.24 eV for 1 M and 3 M, respectively. On the other hand, those on Pt-coated glass substrates are 3.22 eV 3.21 eV for 1 M and 3 M, respectively. Clearly, the energy band gap of samples on Pt-coated are less than those on plain glass substrates. This might be due to the fact that Platinum is a good conductor. Clearly, the energy band gap of samples on Pt-coated are less than those on plain glass substrates.

This might provide an additional insight on why samples on plain glass detect more H₂O₂ during exposure than those on Pt-coated (refer to Fig. 5). This may suggest that electron-hole recombination prefers more to take place in Pt rather than in ZnO. And so, Oxygen anions may have lesser numbers on Pt-coated samples because of lesser number of electrons passing through ZnO at the surface. Thus, lesser change in resistance during the H₂O₂ exposure.

![Figure 7. UV-Vis spectra of annealed samples.](image)

5.3. XRD
XRD spectra of as grown ZnO samples on plain substrate are shown in Figure 8. The peaks of XRD patterns correspond to those of the theoretical ZnO patterns from JCPDS data file, with hexagonal wurtzite structure of the bulk and lattice constants: \(a = 3.24982\ \text{Å}, \ c = 3.26064\ \text{Å}\).

Some of the characteristic peaks with their corresponding indices and interplanar distances in each sample are listed in tables 1 (for 1 M) and 2 (for 3 M).

![Figure 8. XRD Spectra of as grown ZnO on plain glass substrates.](image)

On each sample, three peaks are more pronounced than the rest. These three peaks correspond to (100), (002), and (101) directions of crystallization of wurtzite ZnO nanorods. This suggests that the crystallites are highly oriented with these directions and that the growth along the directions a, b, and

---

3From this point onwards, the notation 1 M means sample from chemical bath whose NH₄OH was 1 M, and the same for notation 3 M, from bath with 3 M NH₄OH.
c-axis are favored. In the diffraction spectra, the intensity ratio in the direction of a axis and c axis (Ia/Ic) and the intensity ratio in the direction of b axis and c axis are useful. These intensities and intensity ratios are listed in table 3.

Table 1. The X-ray diffraction data results of as grown ZnO on plain glass (1 M).

| Peak no. | Indices (hkl) | 2θ[deg] | d[Å]  |
|----------|---------------|---------|-------|
| 1        | (100)         | 32.433  | 2.7604|
| 2        | (002)         | 35.110  | 2.5559|
| 3        | (101)         | 36.919  | 2.4347|
| 4        | (102)         | 48.204  | 1.8878|
| 5        | (110)         | 57.210  | 1.6102|
| 6        | (103)         | 63.498  | 1.4650|

Table 2. The X-ray diffraction data results of as grown ZnO on plain glass (3 M).

| Peak no. | Indices (hkl) | 2θ[deg] | d[Å]  |
|----------|---------------|---------|-------|
| 1        | (100)         | 32.396  | 2.7635|
| 2        | (002)         | 35.075  | 2.5583|
| 3        | (101)         | 36.886  | 2.4368|
| 4        | (102)         | 48.176  | 1.8888|
| 5        | (110)         | 57.001  | 1.6156|
| 6        | (103)         | 63.478  | 1.4654|

As the concentration of NH₄OH of the bath was increased from 1 M to 3 M, the values of Ia/Ic and Ib/Ic also increase. This suggests that there are some differences in the aspect ratios of the nanorods in these samples. Specifically, nanorods in 3 M sample are wider than those in sample 1 M.

| Sample (as grown, plain substrate) | Ia (100) | Ic (002) | Ib (101) | Ia/Ic | Ib/Ic |
|-----------------------------------|---------|---------|---------|-------|-------|
| 1 M                               | 594     | 812     | 886     | 0.73  | 1.09  |
| 3 M                               | 690     | 398     | 632     | 1.73  | 1.59  |

6. Conclusion
In conclusion, ZnO were successfully grown on plain and Pt-coated glass substrates. All of the synthesized samples were able to detect H₂O₂ gas as verified by the sensitivity measurement. The resistance of the samples increases during exposure to H₂O₂ gas and can be used as the basis in detecting H₂O₂. Samples on plain glass substrates have greater capability in sensing and samples on Pt-coated have greater recovery after exposure. UV-Vis spectra show that the energy band gap are in the range of the documented values of ZnO [12,13], with ZnO samples on Pt-coated having less values than those of samples on plain substrate. XRD patterns and data further illustrate that ZnO signature peaks are present in the spectra. This suggests that ZnO was indeed really grown. This further shows that the ZnO nanorods from bath containing 3 M NH₄OH were wider than those from 1 M.

7. References
[1] Klapes N A and Vesley D 1990 Applied and Environmental Microbiology 56 502–3
[2] Webb B C 2001 Journal of Pharmaceutical Science & Technology 55 49–50
[3] Retrieved from http://chemistry.about.com/cs/howthingswork/a/aa101203a.htm
[4] Retrieved from http://www.earthclinic.com/Remedies/hydrogen_peroxide_general.html
[5] Fox et al. 2002 Agency for Toxic Substances and Disease Registry 772 1–3
[6] Hart P W and Rudie A W 2007 TAPPI EPE Conference 34 25233–5
Acknowledgement

The authors would like to thank Prof. Rosemarie Terio of Physics Department of MSU-Main, and Mr. Alnasser Kasim of Turkish Chamber of Commerce Of the Philippines and Miss Christine Adelle Rico for helping the researchers in obtaining the XRD data.

The authors also acknowledge Prof. Bianca Rae Sambo, Prof. Majvell Odarve, Prof. Joy Cristy Piagola, Prof. Jess Gambe of the Physics Department of MSU-IIT for their assistance in this study.