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Effect of Annealing Time Process on the pH Sensitivity of Spin-coated TiO$_2$/ZnO Bilayer Film

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Abstract. This paper presents an investigation on titanium dioxide (TiO$_2$) and zinc oxide (ZnO) bilayer film, which is used as sensing membrane for extended-gate field effect transistor (EGFET) for pH sensing application. TiO$_2$/ZnO thin films were deposited using sol-gel spin coating method on indium tin oxide (ITO) substrates. After the deposition, the bilayer films were annealed at constant temperatures which is 400 °C for 15, 30, 40 and 60 minutes. The sensitivity of the TiO$_2$ thin film towards pH buffer solution was measured by dipping the sensing membrane in pH4, pH7 and pH10 buffer solution. By varying the annealing time, we found that the TiO$_2$/ZnO thin film annealed at 400 °C for 15 minutes gave the highest sensitivity compared to other annealing conditions, with the value of 64.87 mV/pH.

1. Introduction
Chemical sensors with metal oxides as sensing materials play important roles in industrial, medical, domestic and many more applications. Among the chemical sensor existed, pH and gas sensor have been widely investigated and applied due to their importance. For instance, the used of pH sensor was implemented in biomedical [1]. In biomedical field, pH sensor was utilized as blood monitoring, clinical detection and many more [2].

Researchers nowadays are focusing on EGFET [3]–[6], which is a type of pH sensor. This EGFET was designed as an alternative way to overcome the drawbacks of Ion Sensitive Field effect transistor (ISFET). EGFET was chosen because it can be characterize using simple connection and also flexibility of the extended gate design [7]. Other than that, EGFET has few advantages which is low cost, simple in packaging, and better-long stability [3].

In order to fabricate and prepare the EGFET sensing membrane, researchers usually choose metal oxides to be deposited. According to previous researches, vanadium oxide (V$_2$O$_3$) [8], tin dioxide (SnO$_2$) [9], titanium dioxide (TiO$_2$) [10] and zinc oxide (ZnO) [11] were used to be fabricated as sensing membrane. In comparison, between all the chosen metal oxides, ZnO and TiO$_2$ are most...
favorable among researchers because of their performance. These two metal oxides have similar characteristics. Both of these metal oxides are chemically stable and have wide band gap. According to these characteristics, we choose ZnO and TiO$_2$ as the metal oxides as our sensing membrane for EGFET.

In this investigation, we fabricate bilayer film as the sensing membrane for our EGFET by using spin-coating technique. TiO$_2$ act as the upper layer while ZnO act as the lower layer. The characteristics of this bilayer film towards drying temperature was explored and characterized by EGFET measurement, and current-voltage (I-V).

2. Methodology

In this experiment, the glass substrates, which is ITO/glass was first cut into 1 x 2 cm. Then, the substrates were cleaned using standard organic cleaning method with methanol and distilled water, followed by drying with argon gas. After that, the substrates were sonicated (sonic temperature is 40˚C) for 10 minutes with the temperature was set to 50˚C.

2.1. ZnO sol-gel preparation

The solution were prepared by using zinc acetate dehydrate (Zn(CH$_3$COO)$_2$2H$_2$O) as starting material, 2-methoxyethanol (C$_6$H$_8$O$_2$) as a solvent and monomethanolamine (MEA, C$_2$H$_7$N$_4$) as a stabilizer. Zinc acetate was dissolved in a mixture of 2-methoxyethanol and MEA solution to produce 0.4M solution concentration. This solution was stirred at 300 rpm and heated at 80˚C for 3 hours. In order to obtain a clear and homogenous solution, this solution was kept aging for 24 hours at room temperature.

2.2. TiO$_2$ sol-gel preparation

The 0.4M TiO$_2$ sol-gel solution was prepared by mixing two separate solutions (Solution A and B). For solution A, absolute ethanol (C$_2$H$_5$OH), glacial acetic acid, GAA (CH$_3$COOH) and titanium isoproxide, TTIP (Ti(OCH$_2$CH$_2$CH$_2$CH$_3$)$_4$) were used in the solution preparation process. For solution B, the chemicals used were absolute ethanol (C$_2$H$_5$OH), triton X-100 (C$_14$H$_22$O(C$_2$H$_4$)n n=9-10) and deionized water. Both of these solutions were stirred separately for 1 hour at 2000 rpm. Then the stirring process for 1 hour was continued after the solutions were mixed up together.

2.3. TiO$_2$/ZnO bilayer deposition

The fabrication of these bilayer films was conducted by using spin-coating technique at room temperature. The deposition process was conducted by dropping ten drops of TiO$_2$ solution onto ITO/glass substrate at 3000 rpm of spin speed for 60s. After that, the deposition process continued by dropping the ZnO solution onto the TiO$_2$ layer with the same drops, spin speed and duration of speed. Then, the bilayer film was annealed at 400˚C for 15 minutes. The steps were repeated and the annealing time were varied for 30, 45 and 60 minutes.

2.4. EGFET measurement and characterization

The measurement process of TiO$_2$/ZnO bilayer film was done by connecting the bilayer film to the gate pin of commercialized MOSFET NDP6060L by using copper wire to form the extended gate of EGFET setup. Then, the MOSFET was connected to a readout interfacing circuit (ROIC). Kapton tape and silver paste were used as bonding agent between wire and substrate. The sensitivity of the bilayer film towards pH was done by dipping the fabricated sensing membrane with reference electrode (Ag/AgCl) into three different pH value, pH4, pH7 and pH10. The value of the sensitivity was obtained from the slope of the graph plotted. All of the fabricated TiO$_2$/ZnO bilayer films were characterized by using I-V characterization.
3. Result and discussion

3.1. Sensitivity of the TiO$_2$/ZnO bilayer film towards pH buffer solution

Sensitivity is defined as the slope of the output characteristic curve or, more generally, the minimum input of the value of $V_{out}$ and sensitivity of the thin film physical parameter that will create a detectable output change. Table 1 below shows the sensitivity and linearity values for each of the bilayer films, annealed at different annealing time.

According to the result obtained, TiO$_2$/ZnO bilayer film annealed for 15 minutes produced highest sensitivity and linearity value towards pH buffer solution which is 64.87 mV/pH and 0.9776. Comparing with all of the results, sensitivity and linearity value for the bilayer film shows the decreasing trend with the increasing annealing time. TiO$_2$/ZnO bilayer film annealed at longest annealing duration exhibit lowest sensitivity and linearity which is 47.56 mV/pH and 0.9100. We plotted the graph in Figure 1 in order to define the sensitivity and linearity differences between all the bilayer films.

Based on this comparison, we assume that 15 minutes is the optimum annealing time for this bilayer film. According to N.S Kamarozaman et.al, longer annealing duration will produced more oxygen vacancies [12]. Commonly, pH buffer solution contained of H$^+$ and OH$^-$, depends on its value. Due to the positively charged of oxygen vacancies, the TiO$_2$/ZnO bilayer film will attract the OH$^-$ ion that contained in the pH buffer solution. So that, this bilayer film becomes less sensitive towards H$^+$ ion that contained in the pH buffer solution. We can conclude that bilayer film annealed at less time produced highest sensitivity due to the less oxygen vacancies. So that it can attract more H$^+$ ions in the pH buffer solution.

<table>
<thead>
<tr>
<th>Annealing Time (min)</th>
<th>Sensitivity (mV/pH)</th>
<th>Linearity</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>64.87</td>
<td>0.9776</td>
</tr>
<tr>
<td>30</td>
<td>56.60</td>
<td>0.9750</td>
</tr>
<tr>
<td>45</td>
<td>49.63</td>
<td>0.9400</td>
</tr>
<tr>
<td>60</td>
<td>47.56</td>
<td>0.9100</td>
</tr>
</tbody>
</table>

Figure 1 : Sensitivity and linearity comparison each of the TiO$_2$/ZnO bilayer films
3.2. Characterization of TiO$_2$/ZnO bilayer film

3.2.1. Atomic Force Microscopy (AFM) characterization

![AFM images](a) & (b)

Figure 2: AFM result for TiO$_2$/ZnO bilayer film annealed for (a) 15 minutes and (b) 30 minutes.

Figure 2 above shows the AFM result for TiO$_2$/ZnO bilayer film at two different annealing times. According to this figure, we can see the different topology when the annealing time increased. In comparison, TiO$_2$/ZnO bilayer film annealed for 15 minutes produces a uniform and high porosity surface. When annealing time was increased to 30 minutes, the topology and surface changed into less uniform and lower porosity. From this, we assume that when the annealing time increased, the surface and topology of the TiO$_2$/ZnO bilayer will have less uniformity and decreased in porosity. This conditions have support the sensitivity result that obtained in the EGFET measurement. We can conclude that bilayer film that has a uniform and high porosity produced the highest sensitivity and linearity value.

3.2.2. Field Emission Scanning Electron Microscope (FESEM) characterization

![FESEM images](a) & (b)

Figure 3: Surface morphology of TiO$_2$/ZnO bilayer film annealed for 15 minutes at different magnification (a) 50,000x and (b) 100,000x

The surface morphology of TiO$_2$/ZnO bilayer film annealed for 15 minutes was shown in Figure 3. This figure shows the different magnification of the TiO$_2$/ZnO surface morphology. From this figure, TiO$_2$ has been observed on the surface of the bilayer film. The agglomeration of the TiO$_2$ also was observed. However, this agglomeration doesn’t give a huge effect towards sensitivity value. Thus, it is proved that TiO$_2$ had been successfully deposited onto the ITO substrate and become as sensing membrane for the EGFET.
4. Conclusion
In conclusion, TiO$_2$ and ZnO were successfully deposited onto the ITO substrate as the bilayer film. It was proved that annealing time process will influenced the sensitivity of the bilayer film towards pH buffer solution. In this investigation, we successfully fabricate TiO$_2$/ZnO bilayer film that produces highest sensitivity when annealed at less annealing time, which is 15 minutes. The result obtained is 64.87 mV/pH and the linearity is 0.9776. This result was supported with the AFM result, which is a uniform surface topology was observed for TiO$_2$/ZnO bilayer annealed for 15 minutes.

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