Drying Temperature Dependence of Sol-gel Spin Coated Bilayer Composite ZnO/TiO₂ Thin Films for Extended Gate Field Effect Transistor pH Sensor

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Abstract. This study presents an investigation on zinc oxide (ZnO) and titanium dioxide (TiO₂) bilayer film applied as the sensing membrane for extended-gate field effect transistor (EGFET) for pH sensing application. The influences of the drying temperatures on the pH sensing capability of ZnO/TiO₂ were investigated. The sensing performance of the thin films were measured by connecting the thin film to a commercial MOSFET to form the extended gates. By varying the drying temperature, we found that the ZnO/TiO₂ thin film dried at 150°C gave the highest sensitivity compared to other drying conditions, with the sensitivity value of 48.80 mV/pH.

1. Introduction
Extended Gate Field Effect Transistor (EGFET) is gaining much interest as an alternative to Ion Selective Field-Effect Transistor (ISFET) [1-3], to isolate the FET from the chemical environment [4]. The extended gate is a chemically-sensitive membrane, deposited on the signal line extended from the FET gate electrode [5]. EGFET have been applied in many applications, especially as pH sensor [6-8]. While ISFET and EGFET have the same surface ion adsorption mechanism for the pH sensing [9], compared with the ISFET, EGFET has many advantages, such as temperature and light insensitivity, low-cost, simpler to passivate and package, and better long-term stability [10].

Metal oxides are being used as the sensing layer for both ISFET and EGFET. The first pH-sensitive membrane used was silicon dioxide (SiO₂), which was applied to ISFET [11]. Metal oxides such as others are tin oxide (SnO₂) [14][12], ruthenium oxide (RuO₂) [5], zinc oxide vanadium oxide (V₂O₅) [17][13] and carbon-nanotube (CNT) [18][14] were chosen in earlier...
investigations of EGFET pH sensor. Other than that, titanium dioxide [15-16] and zinc oxide [17-18] also has drawn an attraction to be applied as the sensing materials for EGFET pH sensor. All of these materials were chosen due to their pH-sensitive properties. These sensing materials can be deposited by using various methods such as RF Sputtering [19], thermal chemical vapour deposition (TCVD) [15], RF Magnetron Sputtering [20], sol-gel spin-coating technique [21-22]. However, there are numerous study on single metal oxide deposited as the sensing membrane for pH sensor application [22-26]. E. M. Guerra et.al in her study reported that the single TiO$_2$ used as the sensing membrane for EGFET based pH sensor application produced the sensing capability of 47.8 mV/pH [27]. This sensing membrane was fabricated by using sol-gel spin coating technique.

Additionally, nanostructured ZnO that was prepared by using electroless metal deposition (EMD) and atomic layer deposition (ALD) was also applied as the sensing membrane for EGFET, where this sensing membrane produced 46.2 mV/pH sensitivity value [28]. In the literatures however, there are no reported works regarding usage of ZnO/TiO$_2$ bilayer structure as a pH sensing membrane. To further increase the sensor sensitivity, in this work, the combination of two metal oxides for the sensing layer, namely ZnO and TiO$_2$ was explored. Besides the sensing characteristics, the physical properties of the ZnO/TiO$_2$ bilayer film was also investigated.

2. Methodology

2.1. ZnO and TiO$_2$ sol-gel preparation

There are few important steps involved in this experimental. The first step was preparation of ZnO solution. In order to obtained 0.4M solution concentration, zinc acetate dehydrate (Zn(CH$_3$COO)$_2$2H$_2$O) as starting material was dissolved in 2-methoxyethanol solvent and methanolamine (MEA, C$_2$H$_7$N$_4$) stabilizer. The molar ratio of MEA to zinc acetate was 1.0M. This solution was stirred at 300 rpm while heated 80 °C for 3 hours. TiO$_2$ sol-gel solution was prepared using absolute ethanol, glacial acetic acid, titanium isopropoxide, Triton X-100 and deionized water to form a 0.1M solution. The detailed recipe for TiO$_2$ sol-gel solution has been reported elsewhere [29].

2.2. Deposition process

For deposition of the sensing layer, ten drops of TiO$_2$ solution were deposited on the ITO coated glass substrate followed by ten drops of ZnO solution. In between the first and second layer deposition, the thin film was dried at room temperature for 10 minutes. In this work, the drying temperature was varied from room temperature (as deposited) until 150°C. The deposited bilayer thin films were then annealed for 15 minutes at 400°C. The configuration of the deposited ZnO/TiO$_2$ bilayer film is shown in Fig. 1 (a) below. The annealed thin film was then connected to a copper wire to form the extended gate of a commercialized FET incorporated in a readout interfacing circuit (ROIC). For pH sensing measurement, the extended gate was dipped in pH buffer solution, with the setup shown in Fig. 1 (b). A commercialized Ag/AgCl reference electrode was employed in the measurement. The thin films were also characterized by atomic force microscope (AFM), field emission scanning electron microscope (FESEM) and also energy dispersive x-ray spectroscopy (EDX).
3. Results and discussion

Fig. 2 shows the pH sensitivity dependence on the drying temperature. The sensitivity is derived from the slope of the ROIC output voltage versus pH graph. It can be seen that the sensitivity increases with the drying temperature. The detailed values are tabulated in Table 1. Table 1 also shows the thickness of each thin film which decreases as the drying temperature increase. The sensitivity values ranged from 35 to 48 mV/pH while the thickness ranged from 28 to 63 nm. The linearity also is higher for thinner film compared to the thicker ones with the highest is 0.985.

The drying or pre-heating process alters the surface of the thin film [2] that influences the roughness and thickness value [30]. Drying process is important to remove the excessive solvent, moisture and residual chemicals contained in the ZnO and TiO₂ solution during the deposition process. In this study, the solvent used are 2-methoxyethanol and absolute ethanol, which have the boiling of 125°C and 78.3°C respectively. It is crucial to find a suitable and optimum drying temperature because the solvent and stabilizer required to be vaporized. In this study, ZnO/TiO₂ bilayer film dried at 150°C produced highest sensitivity due to the completion of the solvent removal during the drying process. If the temperature is lower than these boiling points, the vaporization and removal process are not complete and will be retarded [31]. This condition will lead to the abrupt vaporization during the annealing process [32]. However, if the temperature is too high, it will cause the solvent to vapor abruptly during the drying process.
Figure 2: (a) Zn/TiO$_2$ composite bilayer thin film configuration deposited by using sol-gel spin coating technique and (b) EGFET pH sensor measurement setup

Table 1. Sensitivity and linearity values for each bilayer film annealed at different duration

| Annealing temperature (°C) | Sensitivity (mV/pH) | Linearity | Thickness (nm) | Surface roughness (nm) |
|---------------------------|---------------------|-----------|----------------|-----------------------|
| Room temperature          | 35.13               | 0.9696    | 63.42          | 45.36                 |
| 50                        | 37.67               | 0.9800    | 51.29          | 25.04                 |
| 100                       | 44.15               | 0.9840    | 37.20          | 25.53                 |
| 150                       | 48.80               | 0.9850    | 28.98          | 2.90                  |

To prevent this condition, the drying process need to be done under a suitable temperature, and this deposition process will be completed with the annealing process, after the drying process done. It is generally known that annealing improves the quality of the thin films. From Table 1, higher drying temperature resulted in lower surface roughness. From these results it can be said that better quality of the film improves the pH sensing characteristics of the ZnO/TiO$_2$ bilayer thin films. Fig.3 (a), (b), (c) and (d) are the three dimensional (3D) topographical images of each ZnO/TiO$_2$ bilayer films obtained from AFM imaging. ZnO/TiO$_2$ bilayer film dried at highest temperature produced smallest roughness value which is 2.90 nm. In comparison, the roughness value for the bilayer film decrease when the drying temperature was raised up to 150 °C and it can be seen that the thin film is more uniform compared to the others. This thin film exhibited the highest sensitivity and linearity when it was used as the sensing layer for the EGFET pH sensor.
Figure 3: AFM topography of ZnO/TiO$_2$ thin film dried at (a) room temperature, (b) 50 °C, (c) 100 °C, and (d) 150 °C respectively.

Figure 4: (a) Surface morphology of ZnO/TiO$_2$ thin film, observed by FESEM and (b) Elements contained on the thin film, characterized by EDX characterization.

On the other hand, Fig. 4 (a) present the surface morphology of the ZnO/TiO$_2$ bilayer film deposited at 3000 rpm. From the image, it can be seen that ZnO had been deposited successfully with uniform surface structure. In addition, Fig. 4 clearly showed that the entire surface was covered with the ZnO, as the top material for this bilayer film. However, only ZnO surface morphology can be observed by FESEM due to its function as the upper layer for this bilayer film. Other than that, it was confirmed that ZnO and TiO$_2$ were successfully deposited based on the EDX characterization. The EDX characterization, which shows in Fig. 4 (b) prove that all of the desired materials, which is ZnO and TiO$_2$ were deposited and exist on the substrate used. EDX result describe that ZnO was dominant, compare with the TiO$_2$. However, TiO$_2$ is still dominant with the other elements existed, such as silicon (Si), tin (Sn), indium (In), nitrogen (N), and also oxygen (O$_2$). Elements such as Si, Sn and In were from the substrate used, ITO coated glass, but elements like N and O$_2$ might originate from the air ambient and environment contamination during the annealing process.

4. Conclusion

ZnO/TiO$_2$ bilayer composite thin films have been successfully deposited on ITO coated glass substrate. The deposited bilayer composite thin film has been proven to be sensitive towards pH. The pH sensitivity of the thin films depends on the drying temperature in which, increasing drying temperature improved the sensitivity. The highest sensitivity achieved in this work was 48.80 mV/pH with the linearity of 0.9850. Higher drying temperature process results in better quality of the thin film. Instead of sensing performance, physical properties of ZnO/TiO$_2$ bilayer film was also improved with the increasing drying temperature, which support the finding from the EGFET measurement.
Acknowledgement

The authors would like to thank all members of NANO-ElecTronic Center (NET) and NANO-Science Center (NST) Universiti Teknologi MARA, UiTM for all the research facilities. The work is partially supported by the Ministry of Higher Education Malaysia under Niche Research Grant Scheme, (600-RMI/NRGS 5/3 (7/2013)).

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