Jurnal
Teknologi

Full Paper

# CHARACTERIZATION OF ZnO/TiO2 BILAYER FILM FOR EXTENDED GATE FIELD-EFFECT TRANSISTOR (EGFET) BASED pH SENSOR

**Article history**
Received
*10 October 2015*
Received in revised form
*21 December 2015*
Accepted
*19 January 2016*

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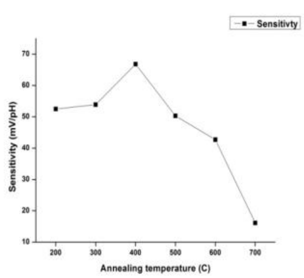



## Abstract

An extended gate field-effect transistor (EGFET) of $ZnO/TiO_2$ bilayer film as pH sensor was demonstrated in this paper. The sol-gel zinc oxide (ZnO) and titanium dioxide ($TiO_2$) were prepared and spin coated onto indium tin oxide (ITO) coated glass substrate. After deposition process, this bilayer film then was annealed from $200^0$ C up to $700^0$ C. EGFET measurement employed to obtain the sensitivity of the bilayer thin film towards pH buffer solution, which is pH4, pH7 and pH10. According to the measurement process, we obtained that bilayer film annealed at $400^0$ C produced highest sensitivity among other bilayer film, which is 66.8 mV/pH.

*Keywords*: Bilayer film; deposition process; anneal; sensitivity;



## 1.0 INTRODUCTION

Over recent years, pH sensing is required in various fields such as biomedical, biosensor, food and health environment and of the most reported sensor type for pH sensing is the ion-sensitive field effect transistor (ISFET) sensor [1] . However, due to some drawbacks of ISFET, Extended-gate FET (EGFET) sensor has been designed as an alternative. EGFET was designed to isolate the sensing FET from chemical environment [2] to overcome the instability problems of ISFET. Comparing with ISFET, EGFET has some advantages which are light insensitive, simple to passivate and package, and stable [3]. EGFET is more stable compared to ISFET because only the sensing membrane will dipped in the measure and instead of the whole FET as for ISFET [4].

In order to fabricate the sensing membrane for EGFET, there are a lot of sensing materials that have been used such as palladium oxide (PdO) [5], tin oxide (SnO) [6], titanium dioxide ($TiO_2$) [7] and also zinc oxide (ZnO) [8]. However, among these materials, $TiO_2$ has been widely used in pH sensing field due to its advantages and capability. Besides that, $TiO_2$ also has been used in numerous applications such as cosmetics, dye, paints and others. $TiO_2$ has been considered as a useful material because of its wide band gap, good stability at high temperature, chemical durability and mechanical abrasion [7].

Other than that, researchers have been extensively studied on ZnO due to their dual properties, which are semiconducting and piezoelectric materials. These properties make ZnO thin films demonstrated to have enormous applications in sensing application, transparent electronic, ultraviolet (UV) light emitter, optoelectronic, chemical sensor, piezoelectric devices and etc [9] [10]. Furthermore, there is a lot of presented result based on ZnO thin films shows the performance of device is direct connected with the good crystalline structure quality ZnO thin film [11].

Therefore, ZnO and $TiO_2$ have been considered as a suitable couple in order to produce a good thin film for pH sensing application [12]. However, the chemical and physical properties of this ZnO/$TiO_2$ bilayer film are depending on the fabrication and manufacturing method. There are several method that can be used to fabricate the thin film such as physical vapor deposition [13], hydrothermal [14] and sol-gel [15]. Between all of these methods, sol-gel technique is most suitable due to its low cost process with and controllable on the film purity and uniformity.

In this paper, we investigate the ZnO/$TiO_2$ bilayer film which produced by sol-gel method. This bilayer film was annealed at various temperatures which started at 200°C up to 700°C. The deposition process was done using spin coating technique. Then, the bilayer film was used as pH sensing membrane. This sensing membrane also has been characterized in order to explore its characteristics.

## 2.0 EXPERIMENTAL

In this investigation, there were two separate solutions prepared which are $TiO_2$ and ZnO solution. Both of these solutions were deposited onto Indium Tin Oxide (ITO), which act as the substrate. Sol-gel method has been used and the deposition process was done by using spin-coating technique in order to deposit the bilayer film.

### 2.1 $TiO_2$ Sol-Gel Peparation

The 0.4M $TiO_2$ sol-gel solution was prepared by mixing two separate solutions (Solution A and B). For solution A, absolute ethanol ($C_2H_5OH$), glacial acetic acid, GAA ($CH_3COOH$) and titanium isoproxide, TTIP ($Ti(OCH_2CH_2CH_2CH_3)_4$) were used in the solution preparation process. For solution B, the chemicals used were absolute ethanol ($C_2H_5OH$), triton X-100 ($C_{14}H_{22}O(C_2H_4)_n$ 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.

### 2.2 ZnO Sol-Gel Peparation

The solution were prepared by using zinc acetate dehydrate (Zn $(CH_3COO)_2\,2H_2O$) and aluminium nitrate ($Al(NO_3)_3$) as starting material, 2-methoxyethanol ($C_3H_8O_2$) as a solvent and monomethanolamine (MEA, $C_2H_7N_{14}$) 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.

### 2.3 ZnO/$TiO_2$ Bilayer Film 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. Then, the deposition process continued with ZnO solution onto the $TiO_2$ layer with the same drops, spin speed and duration of speed. After that, this bilayer film was annealed at 200°C, 300°C, 400°C, 500°C, 600°C and 700°C. The annealing time was fixed at 15 minutes.

### 2.4 EGFET Measurement And Characterization

The ZnO/$TiO_2$ bilayer film was then connected to the gate pin of commercialized MOSFET NDP6060L by using copper wire to form the extended gate of EGFET sensor 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 s lop of the graph plotted. All of the fabricated ZnO/$TiO_2$ bilayer films were characterized by using Field Emission Scanning Electron Microscope (FESEM), Atomic Force Microscopy (AFM) and X-Ray Diffraction (XRD). Repeatability issue which may be caused by noise was solved by referencing the voltage levels to the sensor response in deionized water (DIW) [16][17] [18].

## 3.0 RESULTS AND DISCUSSION

### 3.1 Sensitivity of the Bilayer Film

Sensitivity can be defined as the slope of the output characteristic curve or 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 [2]. In this investigation, the sensitivity of ZnO/$TiO_2$ bilayer films was estimated from the slope of the $V_{out}$ vs pH graph. The numerical results are tabulated in Table 1.

Figure 1 shows the annealing temperature dependence of the sensitivity. As can be seen, $ZnO/TiO_2$ bilayer film annealed at 400°C exhibit highest sensitivity which is 66.8 mV/pH. However, this value of sensitivity can be classified as super-Nernstian response since the theoritical Nernst value for EGFET is 59.12 mV/pH [19]. The super-Nernstian response is related to the reactive mechanism of one transport electron per 1.5 $H^+$ ion [20]. According to this, we assumed that there are more than one proton react with one electron contained in the solution.

Sensitivity of the bilayer film shows an increase trend when annealed at 200°C-400°C. However, the sensitivity decreased when sample annealed at 500°C

**Table 1** Sensitivity value for each of bilayer film

| Annealing Temperature (°C) | Sensitivity (mV/pH) |
|---|---|
| 200 | 52.5 |
| 300 | 53.9 |
| 400 | 66.8 |
| 500 | 50.3 |
| 600 | 42,7 |
| 700 | 16.1 |

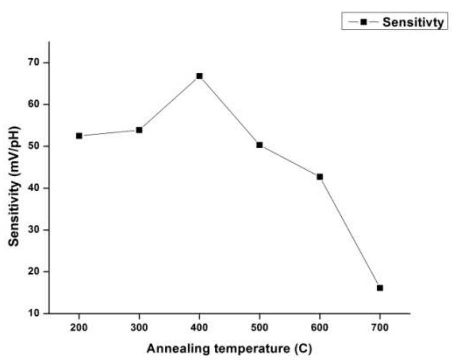



**Figure 1** Sensitivity comparison between all $ZnO/TiO_2$ bilayer films

and above. $ZnO/TiO_2$ bilayer film annealed at 700°C exhibit lowest sensitivity value which is 16.1 mV/pH. The bilayer film annealed at suitable and appropriate temperature produced better sensitivity because of the improvement in electrical and material characteristics [21]. Based on this finding, 400°C is the most suitable temperature to anneal this $ZnO/TiO_2$ bilayer film.

From this, we assume that besides the improvement of the materials characteristics, when the thin was film annealed at suitable temperature, all the solvents in the solution were removed and only $TiO_2$ and ZnO were on the thin film [10]. Different with the thin film annealed at low temperature, there were solvents that still contained at the thin film which gave the effects to the sensitivity value. In the other hand, when annealed at too high temperature, the sensitivity of the bilayer film decrease numerously. Yao et. Al proposed that annealing temperature was predominated in pH sensitivity due to its phase transition [2].

### 3.2 Surface Morphology Of The Bilayer Films

The micrographs from FESEM images show that $ZnO/TiO_2$ bilayer films are porous, which is normal phenomenon for sol-gel ZnO thin film [1]. However, there is only ZnO nanoparticle that can be observed, not the $TiO_2$ nanoparticles. This is due to the layer of deposition, which is ZnO act as the upper layer, and $TiO_2$ is bottom layer. According to the micrograph obtained, the size of the particles is increase gradually. The increase in grain size is attributed to the agglomeration due to the increasing annealing temperature [22].

The temperature is believed to give the effect to the grain size of the $ZnO/TiO_2$ bilayer film. Figure 2 shows that the grain size of the bilayer film increases as the annealing temperature increase. This increasing of grain size influenced the bilayer film to become less sensitive towards pH buffer solution.

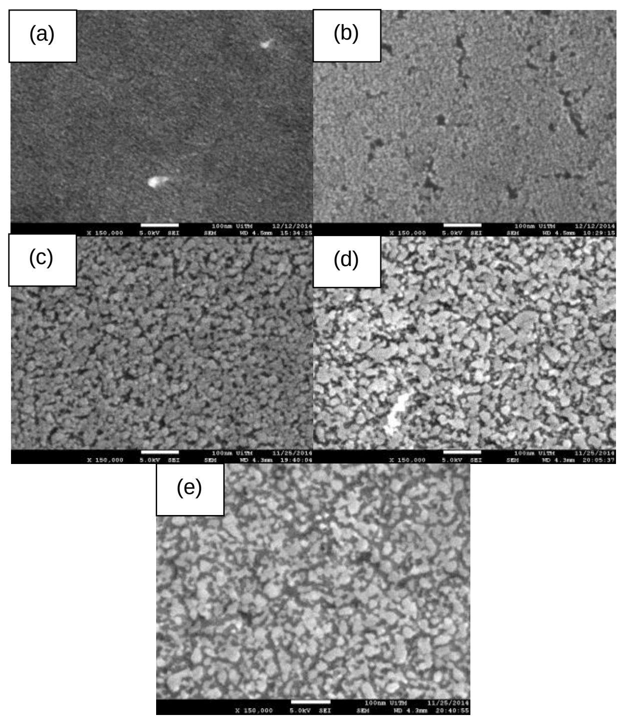



**Figure 2** SEM images for $ZnO/TiO_2$ bilayer film anneal at (a) 300°C, (b) 400°C, (c) 500°C, (d) 600°C and (e)700°C.

### 3.3 Surface Roughness Characterization

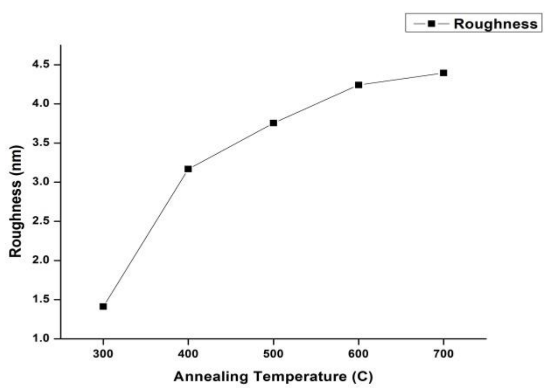
The 3 dimensional images for all of $ZnO/TiO_2$ bilayer film annealed at different temperatures are shown in Figure 3. The 3D images show that the surface morphology and roughness increase with the increase annealing temperature. The roughness values for each bilayer film are recorded in Table 2. From the values recorded, we able to plot the graph in Figure 4 in order to observe the roughness characteristic of each bilayer film.

Among all of the bilayer films, $ZnO/TiO_2$ bilayer film annealed at 400ºC shows a smoother surface in comparison with other samples. In addition, this bilayer film also shows the uniform grain size. According to this, we assume that annealing temperatures influenced the surface smoothness and roughness of the $ZnO/TiO_2$ bilayer film.

Regarding to the result obtained, $ZnO/TiO_2$ bilayer films show an increasing roughness trend with the increasing annealing temperature. This is due to the annealing process, which involved the heat treatment and restructuring process. When annealing temperature increase, the materials deposited were restructured and gave effect towards its surface roughness [23]. This condition gave the effect towards its sensitivity. Bilayer film with the highest roughness produces lowest sensitivity. However, bilayer film with the lowest roughness also produces low sensitivity towards pH solution. Means that, bilayer film with the optimum roughness, which is 3.167 produced highest sensitivity value. This bilayer film was annealed at 400ºC.

**Table 2** The roughness value for $ZnO/TiO_2$ bilayer film anneal at different temperatures

| Annealing Temperature (°C) | Roughness |
|---|---|
| 300 | 1.411 |
| 400 | 3.167 |
| 500 | 3.755 |
| 600 | 4.241 |
| 700 | 4.394 |



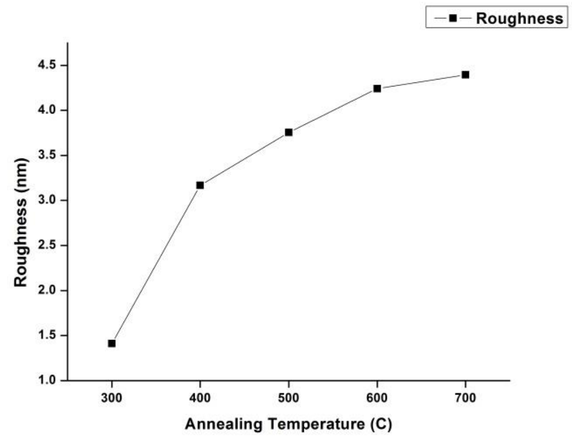




**Figure 3** Roughness comparisons for all samples

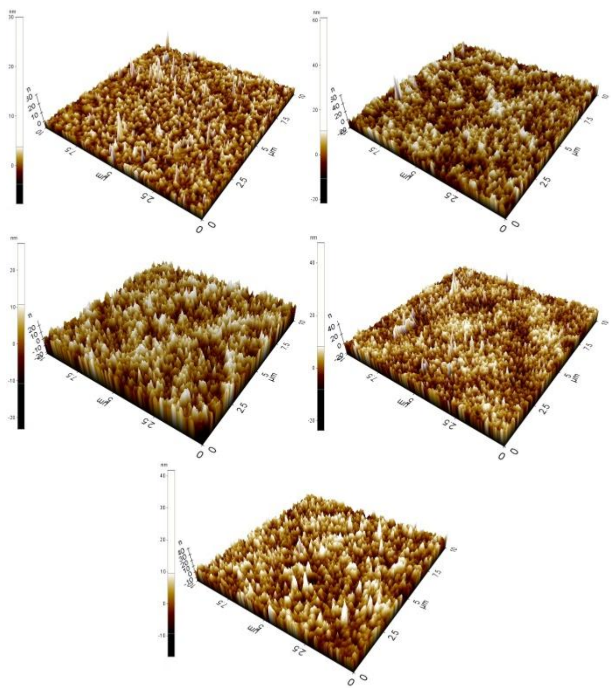


**Figure 4** 3D AFM images of $ZnO/TiO_2$ bilayer film anneal at (a) 300ºC, (b) 400ºC, (c) 500ºC, (d) 600ºC and (e)700ºC

### 3.4 Crystalline Analysis

XRD patterns of the samples annealed at 300ºC, 400ºC and 500ºC are shown in Figure 5. All of the diffraction peaks in the result is according to the standard card (00-036-1451) and (01-076-1940). $ZnO/TiO_2$ bilayer film annealed at 300ºC does not show any dominant peak, so as $ZnO/TiO_2$ bilayer film annealed at 500ºC. Different with $ZnO/TiO_2$ bilayer film annealed at 400ºC, there are few dominant peaks that can be observed. From the result, it can be seen that both ZnO and TiO present in this bilayer film. We can observed that ZnO peak present at 31.15º which is (100), meanwhile $TiO_2$ peak present at 35.82º (101). Due to this peak, we can classify that the $TiO_2$ peak present as rutile phase. Other than that, the other two peaks which present at 50.84 (440) and 60.62 (662) are our substrate which is ITO.

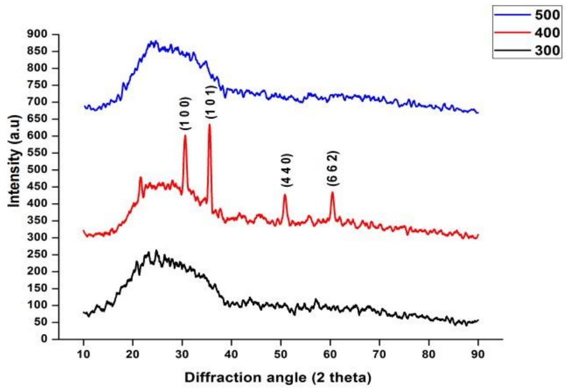



**Figure 5** XRD spectra for $ZnO/TiO_2$ bilayer film annealed at 300°C, 400° and 500°C respectively

According to the result obtained, the XRD analysis supported the sensor performance of the $ZnO/TiO_2$ bilayer. $ZnO/TiO_2$ bilayer film an nealed at 400°C produced highest sensitivity value, and shows the dominant peaks of ZnO and $TiO_2$ in XRD analysis indicating that thin films with better crystalline quality results in higher sensitivity.

## 4.0 CONCLUSION

The characteristics of the $ZnO/TiO_2$ bilayer films anneal at different temperatures were presented in this paper. Zinc oxide and titanium dioxide has been successfully deposited on the IT O substrate by using spin-coating technique. The sensitivity, surface morphology and crystallinity of the bilayer film were observed and determined. According to the measurement process, we obtained that $ZnO/TiO_2$ bilayer film annealed at 400°C exhibit highest sensitivity value which is 66.8 mV/pH. This result was supported with the AFM and XRD characterization. The AFM result for this optimize bilayer present a uniform surface, compare with other bilayer films. For XRD analysis, the crystallinity of the bilayer film was proved with the present of ZnO (100) peak and $TiO_2$ rutile phase (101) peaks. As a conclusion, 400°C was proved as the optimum annealing temperature for $ZnO/TiO_2$ bilayer film.

## Acknowledgement

This study was partially supported by MOE Malaysia under the Niche Research Grant Scheme (NRGS) (Project code: 600-RMI/NRGS 5/3 (7/2013) and Universiti Teknologi MARA (UiTM).

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