Annealing time dependence of the physical, electrical and pH response characteristics of spin coated TiO$_2$ thin films

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Abstract. Titanium dioxide (TiO$_2$) thin film was deposited on indium tin oxide (ITO) substrate and used as sensing membrane of EGFET pH sensor. The thin film was fabricated using sol-gel spin coating method. All samples were annealed at 400 °C but the annealing time was varied. This is done to study the effects of annealing time on physical and electrical properties of titanium dioxide thin film. The sensitivity of each sample towards H$^+$ ion was measured and result shows that sample annealed for 45 minutes has the highest sensitivity (52.6 mV/pH). It is found that increasing annealing duration will increase the pH sensitivity but a limit will be reached at certain point. Longer annealing processes done beyond this point will results in lower pH sensitivity.

1. Introduction

The glass selective membrane electrode is the popular structure for pH sensor. Another well-known structure for pH sensor is ion sensitive field effect transistor (ISFET) [1]. Due to brittleness of the former and device instability of the latter, another pH sensor was proposed. The device is known as extended gate field effect transistor (EGFET) and was first reported by Spiegel in 1983 [2]. It has the same working principal as ISFET since it was developed from it. The main difference between ISFET and EGFET is that the sensing membrane of EGFET is extended from the sensing MOSFET [3]. This extended structure gives few advantages such as device stability, temperature insensitivity and flexibility in designing shape of the extended gate [4-6].

Metal oxides in form of thin films has been investigated to be used as sensing layers to detect presence of H$^-$ ions in solutions. Among them are palladium oxide [7], indium tin oxide [8], silicon dioxide [9], titanium dioxide [10] and zinc oxide [11]. TiO$_2$ is chosen to be used in this experiment since it has many interesting properties such as chemically stable and shows good electrical and optical properties [12-14].
There are several reported ways of depositing titanium dioxide thin films. Examples are chemical vapor deposition (CVD) [15], spin coating [16], chemical bath deposition (CBD) [17], atomic layer deposition (ALD) [18], and magnetron sputtering [19]. Due to its easy handling procedure and good uniformity of thin film fabricated, sol-gel spin coating is more favored compared to the other processes [20-21]. An important factor in controlling the quality of thin films produced is by controlling the post-deposition annealing temperature and time. In this paper, study on effects of increasing annealing time towards sensitivity of TiO$_2$-based EGFET pH sensor was done.

2. Experimental details

ITO substrate was cleaned using methanol and deionized (DI) water in ultrasonic cleaner. The substrate was then dried by blowing with nitrogen gas. TiO$_2$ solution was prepared from mixture of Solution A and Solution B. Solution A comprise of titanium (IV) isopropoxide (precursor), absolute ethanol (solvent) and glacial acetic acid (stabilizer). Solution B contains Triton X-100 (surfactants), deionized water and absolute ethanol (solvent). Solution A and B were stirred for 1 hour. Then both solutions were mixed and the mixture was continued to be stir for another hour.

The cleaned ITO coated glass substrate was spun with the speed of 3000 rpm for one minute. During the spinning process, ten drops of the prepared TiO$_2$ solutions were dropped onto the substrate. The TiO$_2$ solution will disperse evenly throughout the substrate surface as a result of the high speed spinning. The TiO$_2$ (now in form of a thin film) would then be dried at temperature of 200 °C for duration of 10 minutes.

Then the samples were annealed at a temperature of 400 °C. However the duration of the annealing process were varied for each particular sample. First, second, third and fourth sample were all annealed for 15, 30, 45 and 60 minutes respectively. Each sample was labeled based on their respective annealing time. Sample annealed for 15 minutes is named $t_{15}$, 30 minutes is $t_{30}$, 45 minutes is labeled $t_{45}$ and $t_{60}$ is sample annealed for 60 minutes.

The samples were measured for its sensitivity towards sensing H$^+$ ions in solutions. It is done by connecting the sample to the gate of MOSFET. The sample now acts as the gate of the MOSFET which is then attached with readout interface (ROIC) [22] which is linked to a power supply and multimeter. The physical characterization includes of determining thickness of TiO$_2$ thin films that had been annealed at different time. Surface studies of the samples were done by using atomic force microscopy (AFM). Electrical properties of each thin film were also found after analyzing graphs from the resulted I-V measurement.

3. Results and discussion

Surface profiler was used to determine thickness of each sample. The value was taken from average of three readings. Table 1 shows the data obtained. It was shown from the data that increasing annealing time of samples will decrease the thickness of thin film. This might be due to elimination of solvent and organic residues during annealing [23]. It is noteworthy to state that annealing process also would result in densification [24-25] and shrinkage of thin films.

| Annealing time (minutes) | Thickness (nm) |
|--------------------------|----------------|
| 15                       | 30.27          |
| 30                       | 29.65          |
| 45                       | 21.57          |
| 60                       | 15.57          |
AFM is done to measure and obtaining roughness of thin films. Depending on the application, rough surface might be unwanted or required. According to studies done by [26], annealing process may modify the surface of thin films where grain size will increase as well as the surface roughness. The changes in mentioned physical aspects will influence several properties such as electron movement and light scattering [27]. Figure 1 shows AFM images obtained from the samples.

![AFM Images](image1.png)

**Figure 1.** AFM images representing surface roughness of (a) $t_{15}$, (b) $t_{30}$, (c) $t_{45}$, and (d) $t_{60}$

The surface roughness is 2.745 nm, 3.174 nm and 5.359 nm for $t_{15}$, $t_{30}$ and $t_{45}$, respectively. The annealing process conducted in this experiment was found to increase the surface roughness of the thin films. This result is comparable with works by [28-29] where they also reported an increase in the surface roughness of their thin films when annealing process was applied. The roughness however decreases when sample being annealed for 60 minutes. $t_{60}$ has roughness of 2.265 nm.

Besides the physical alteration, annealing would also change the electrical properties of thin films. The TiO$_2$ thin films had been seen to be decreasing in their electrical performance when being annealed as can be seen in the I-V in characteristics in Figure 2. Ohmic characteristic was observed for all samples. Based on data from the graphs, the resistivity and conductivity of each sample was calculated.

![I-V Graph](image2.png)

**Figure 2.** I-V measurement graph
The resistivity, $\rho$ and conductivity, $\sigma$ is shown in Table 2. It can be said that annealing process decreases the electrical conductivity of TiO$_2$ thin film. Further annealing done at a longer period of time will further decrease the conductivity value. Since the resistivity is inversely proportional to conductivity, increase in annealing time would mean an increase in resistivity of thin films.

Electron scattering would be reduced if smoother surface was obtained. The reduction in electron scattering in exchange would increase conductivity of thin films [30]. Considering the facts that annealing process done in this experiment increases the surface roughness of TiO$_2$ thin films, it explains why conductivity of thin films undergoes decline in values.

| Annealing time (minutes) | Resistivity, $\rho$ (\(\Omega\).cm) | Conductivity, $\sigma$ (S.cm$^{-1}$) |
|--------------------------|------------------------------------|-------------------------------------|
| 15                       | 6.68x10$^5$                        | 1.50x10$^6$                         |
| 30                       | 8.20x10$^5$                        | 1.22x10$^6$                         |
| 45                       | 2.20x10$^6$                        | 4.55x10$^7$                         |
| 60                       | 3.04x10$^6$                        | 3.29x10$^7$                         |

The sensitivity measurement resulted in data in form of voltage output. Each voltage output produced at corresponding pH buffer solutions were plotted in Figure 3(a). The graph was then analysed to determine the sensitivity and linearity of each sample. A trend is spotted from the tabulated data and plotted graph. Longer annealing time was seen to improve the sensitivity of TiO$_2$ sensing membrane towards H$^+$ ions in the pH buffer solution. All sensitivity and linearity values were tabulated in Table 3.

![Figure 3](image)

Figure 3. Graphs of (a) output voltage (b) sensitivity of samples fabricated

t$_{15}$ has good sensitivity with value of 45.0 mV/pH. The t$_{30}$ sample which was annealed 15 minutes longer than t$_{15}$ sample has 49.5 mV/pH sensitivity. The sensitivity was further increased when TiO$_2$ thin film was annealed for 45 minutes. t$_{45}$ sample was also the sensing membrane with the highest sensitivity. With sensitivity of 52.6 mV/pH, it has sensitivity approaching Nernstian theoretical value (59 mV/pH).
| Annealing time (minutes) | Sensitivity (mV/pH) | Linearity (%) |
|--------------------------|---------------------|---------------|
| 15                       | 45.0                | 96.33         |
| 30                       | 49.5                | 99.60         |
| 45                       | 52.6                | 98.78         |
| 60                       | 44.6                | 99.24         |

However, there was decrease in sensitivity of TiO$_2$ sensing membrane when the sample being annealed longer than 45 minutes. It is shown when $t_{60}$ sample has lowest sensitivity compared to $t_{45}$ sample and other previous samples. It is concluded that 45 minutes is the ideal annealing time for TiO$_2$ sensing membrane for EGFET pH sensor.

The pattern shown by sensitivity value were the same as pattern observed in roughness value of samples. Annealing time affects the roughness of the samples and these changes in surface roughness was most likely to be the reason behind the increment and decrement of sensitivity of samples. In term of linearity, all sample fabricated shows good sensing performance when being use as sensing membrane. With linearity value of 96.33%-99.60%, TiO$_2$ is proven to be a good material for detecting H$^+$ ions in liquid solutions.

4. Conclusion

Instead of using ISFET structure, TiO$_2$ was integrated as sensing membrane in EGFET structure for pH sensing. Studies on effects of applying different annealing time on fabricated TiO$_2$ thin films were effectively conducted. Each thin film was characterized for its physical and electrical performance. The annealing time was varied from 15 minutes, 30 minutes, 45 minutes and 60 minutes and was labeled as $t_{15}$, $t_{30}$, $t_{45}$ and $t_{60}$ respectively. Physical characterization was completed and first significant finding was that thickness of TiO$_2$ thin films is dependent on annealing time. Samples anneal for 15 minutes, 30 minutes, 45 minutes and 60 minutes has thickness of 30.27, 29.65, 21.57 and 15.57 nm correspondingly. It means that the longer annealing time, the thinner the thin film would be. The TiO$_2$ surface was noticed to gain roughness when being annealed for longer period of time. However it was found that the roughness decreases when the thin film was annealed for 60 minutes.

The second part of characterization focused on electrical characterization. I-V measurement was carried out and I-V characteristics graph was obtained. The graph indicates that all TiO$_2$ sample produced has ohmic characteristic. Data information from the graph was extracted to calculate resistivity, $\rho$ and conductivity, $\sigma$. Resistivity of TiO$_2$ thin films increases when annealing time increases. Conductivity of the samples however decline when longer annealing period was applied. TiO$_2$ was recognized as suitable sensing material to be use in detecting H$^+$ ions in different pH solutions since it has good linearity value of 96.33%-99.60%. $t_{15}$, $t_{30}$, $t_{45}$ and $t_{60}$ have sensitivity of 45.0 mV/pH, 49.5 mV/pH, 52.6 mV/pH and 44.6 mV/pH respectively. Hence it was concluded that 45 minutes is the best annealing time to anneal TiO$_2$ thin films in order for the film to give optimized performance when being used as sensing membrane in EGFET pH sensor.

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