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METAL OXIDE THIN FILMS AS pH SENSING MEMBRANE FOR EXTENDED GATE FIELD EFFECT TRANSISTOR

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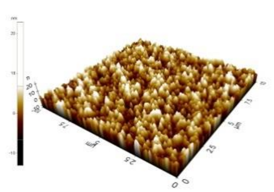
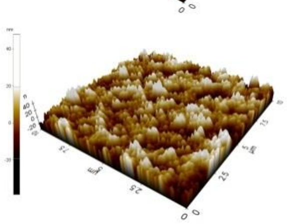
Graphical abstract





Abstract

In this research, metal oxides (ZnO and TiO_2) thin films were fabricated by the sol-gel spin coating method. The thin films were applied as the pH sensing membrane for the extended-gate field effect transistor (EGFET) sensor to distinguish the sensing capability between them. The surface morphology, thin film components and crystalline quality were characterized and the sensor performance of both materials were characterized and compared. The results showed that TiO_2 thin film gave higher sensitivity with better linearity compared to the ZnO thin films hence was considered a more suitable material to be used as sensing membrane in EGFET pH sensor compared to zinc oxide.

Keywords: Metal oxide, titanium dioxide, (EGFET) pH sensor, sensing membrane, sensitivity, sol-gel spin coating, zinc oxide

1.0 INTRODUCTION

Metal oxides are materials with unique properties. It can be fabricated through several deposition techniques. Chemical vapor deposition [1-2}, sputtering [3-4], pulsed laser deposition [5-6], hydrothermal deposition [7-8], and spin coating [9-10] are a few examples. Sol-gel spin coating was one of the most popular deposition techniques due to low cost [11] and easy preparation [12]. Our basic sol-gel preparation involves chemical reaction between metal alkoxide precursor with several others reactant such as acetic acid stabilizer and solvents. Hydrolysis and polycondensation process that occurs during the reaction [13] would results in hydrated metal oxides that would later be deposited in form of solid thin films. There has been a lot of interest among scientists and engineers to explore the usage of metal oxides in their applications. Examples are utilization of metal oxides in sensing devices such as gas sensor [14-15], glucose sensor [16-17] and pH sensor [18-19].

pH sensing is particularly important since many processes and chemical reactions are highly dependence on pH level. The existence of extended gate field effect transistor was considered invaluable since it allows modification on type of metal oxide used as sensing membrane. Metal oxides likes tin oxide [20], zinc oxide [21], palladium oxide [22] and titanium dioxide [23] shows capability in detecting hydrogen ion in solutions thus determining pH value of the solution. Zinc oxide (ZnO) and titanium dioxide (TiO_2) had caught interest since both has excellent chemical properties compared to other metal oxides. To the best of our knowledge, there are no literature specifically doing comparison work on H^+ sensitivity of titanium dioxide and zinc oxide. Thus this paper study the sol-gel spin coated zinc oxide and titanium dioxide thin films for EGFET pH sensor sensing membrane. Two main goals of this research is first to identify the superior material (between TiO_2 and ZnO) to be used as sensing membrane in EGFET pH sensor. Second is to investigate the effects of increasing annealing temperature on sensitivity of TiO_2 and ZnO thin films towards pH.

2.0 EXPERIMENTAL

2.1 Solution Preparation

Solution of ZnO and TiO_2 was prepared. The precursor for ZnO and TiO_2 solution was zinc acetate and titanium (IV) isopropoxide respectively. Zinc acetate was mixed with aluminium nitrate, 2-methoxyethanol and monoethanolamine. The mixture was stirred and heated at 80 °C for 3 hours. Then the stirring was continued for 24 hours at room temperature. For TiO_2 solution, two beakers were used. Beaker A contains TTIP, glacial acetic acid and absolute ethanol. Beaker B has absolute ethanol, Triton X-100 and deionized water. Both beakers were stirred for an hour. Solution B was mixed with Solution A and the mixture was stirred for one hour. Indium tin oxide on glass was cleaned with consecutive ultrasonic cleaning using methanol and DI water. After being rinsed and dried using argon gas, the ITO was used as substrate for ZnO and TiO_2.

2.2 Metal Oxide Thin Film Fabrication

The ZnO solution was deposited on ITO by using sol-gel spin coating method. The substrate was placed on spin coater platform before being spun at 3000 rpm. 10 drop of liquid ZnO was dropped on top of the ITO substrate and spun for one minute. After that, the deposited ZnO thin film was dried at 200 °C for 10 minutes. This would eliminate the solvent residue. The thin film then undergoes annealing process for 15 minutes at 200 °C. This process of solution deposition, drying and annealing was repeated for fabricating TiO_2 thin films.

2.3 EGFET pH Sensor Measurement

Then both ZnO and TiO_2 were used as sensing membrane for EGFET pH sensor. They are connected to gate of MOSFET but extended away from the structure. Incorporating the MOSFET with ROIC [24], power supply and multimeter would complete the pH sensitivity measurement setup. pH buffer solutions used were pH 4, pH 7 and pH 10. First the metal oxides were immersed in pH 4 buffer solution. Then the reading of the output voltage was noted. Three reading was recorded and average reading was taken. The step was repeated for pH 7 and pH 10 buffer solutions. Then the average V_{out} for each solution was plotted in a graph. The slope of the line in the graph represents value of the sensitivity of the sample.

3.0 RESULTS AND DISCUSSION

3.1 Structural Analysis

Surface morphology of both metal oxides was studied using FESEM (Carl Zeiss Supra 40 VP). The thin film structure was observed and the obtained images are shown in Figure 1. Similar surface structure was seen all over TiO_2 thin film. Same distribution pattern was seen on ZnO structure although the type of structure was different. The ZnO thin film contains what seems to be tiny hole-like structure. The uniform distribution of structure on both TiO_2 and ZnO thin film was because of the deposition technique used. Since sol-gel spin coating produce thin film with uniform thickness [25], identical structure of metal oxides would also be spread throughout the thin films.

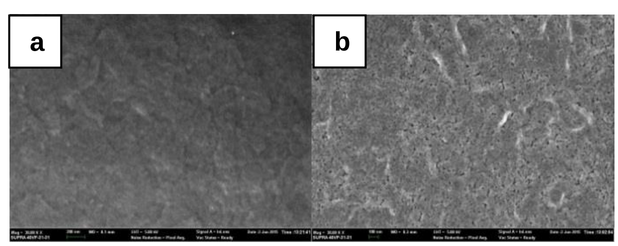


Figure 1 Structure of (a) TiO_2 and (b) ZnO

Fabricated ZnO and TiO_2 were tested with Oxford Instrument Energy Dispersive Spectroscopy (EDS) to analyze elements existed on the thin films. Figure 2 is the results from EDS characterization. ZnO thin film contains zinc, oxygen and indium. For TiO_2 thin film, traces of titanium, oxygen and indium were found. This EDX analysis proves the existence of desired metal element in their respective metal oxides thin films.

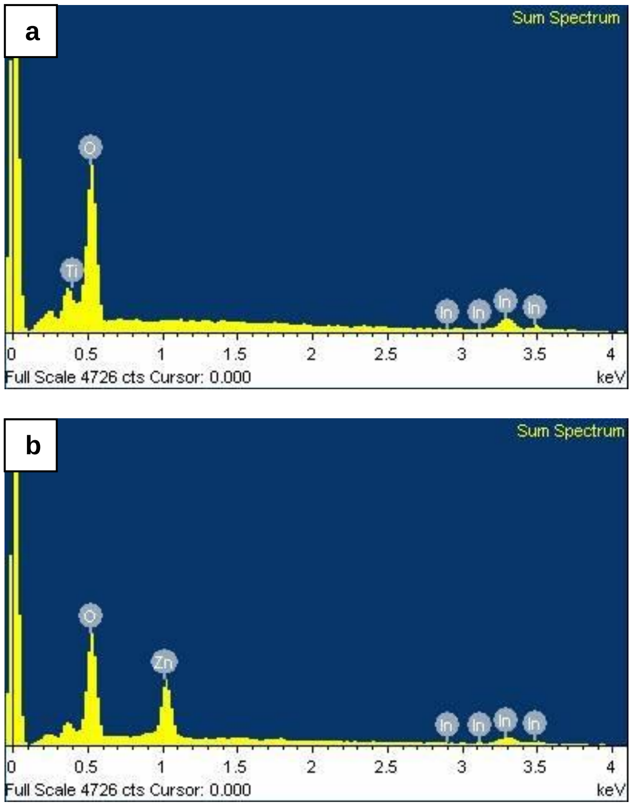


Figure 2 Results of EDS analysis done on (a) TiO_2 thin film and (b) ZnO thin film

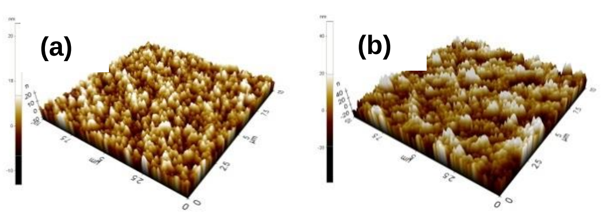


Figure 3 Surface roughness on (a) TiO_2 surface and (b) ZnO surface

Figure 3 above are the images of TiO_2 and ZnO that was taken using AFM (Park Systems XE-100). The TiO_2 thin film was shown to have smaller grain size and lesser roughness values compared with ZnO. TiO_2 has roughness of 2.745 nm while ZnO has rougher film surfaces of 7.792 nm. Roughness is related to particle or grain size of the material. Usually the applied annealing process was assumed to be the main factor in determining the final grain size of the metal oxide thin films [26-29].

Since the annealing temperature for both metal oxides were the same, another possibility was considered. Basic formation of metal oxides starts with nucleation of the precursor followed by growth of the nuclei. It was during aging process that the average particle size increases, following Ostwald ripening phenomenon [30-32]. The solution preparation recipe used in this work is the optimized recipe reported by our group elsewhere [33] thus different parameters were used to prepare both solutions respectively. ZnO solution was aged for 24 hours whereas TiO_2 solution was aged for one hour. Hence the longer aging process of ZnO might be the reason behind larger particle size and roughness of ZnO thin film, in contrast with TiO_2 thin film.

Both thin films were characterized using X-ray diffraction as to check the crystallinity of the produced metal oxides. XRD pattern in Figure 4 is a solid evidence that ZnO and TiO_2 thin films is in crystalline state since amorphous sample would show no peaks. Each material owns their distinctive crystalline structures.

The studies done on TiO_2 XRD graph peaks enable the crystalline structure that made up the sample to be identified. The (1 0 3) crystal orientation found on 2 theta (2Θ) angle of 35.66° indicates that the TiO_2 thin films has anatase phase. Since TiO_2 was in anatase phase, the structure was mainly in tetragonal crystal system [34]. On the other hand, ZnO thin film was confirmed to be in zincite form. Different from TiO_2, the crystal in ZnO was arranged in hexagonal form [35].

Crystalline metal oxides can be achieved if certain conditions were met. Our metal oxide thin films had crystalline structure since the post-deposition annealing process was done at temperature of 400 °C. This temperature was the minimum temperature needed for ZnO and TiO_2 crystal lattice to be rearranged and forming crystalline structure [36].

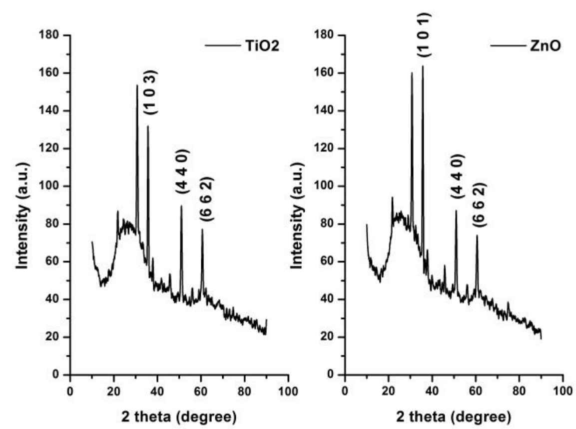


Figure 4 XRD peaks for the metal oxides

3.2 Sensitivity Measurement

The results from pH measurement is graphically plotted in Figure 5. Y-axis is the voltage output (V_{out}) while the pH value of the buffer solutions is the x-axis. From the graph, sensitivity value is taken from the slope of the lines. The linear lines in the graph indicate reliability of both ZnO and TiO_2 to be used in measuring pH [37]. Sensitivity and linearity value for ZnO is 48.3 mV/pH and 98.22% respectively. On the other hand, TiO_2 has sensitivity of 53.0 mV/pH and linearity of 99.02%. The difference in sensitivity between ZnO and TiO_2 was not large. However since TiO_2 still has better sensitivity and linearity than ZnO, the former was considered to be a more suitable material to be used as sensing membrane for EGFET pH sensor compared to the latter.

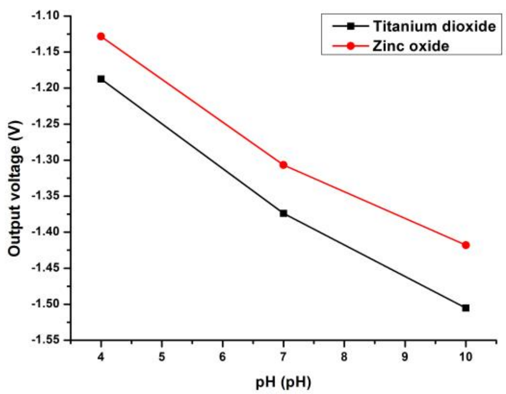


Figure 5 Output voltage of the metal oxides

To further investigate and compare sensing capabilities between the metal oxides, annealing temperature was varied from 300 °C to 500 °C. The annealing period was fixed at 15 minutes. The plotted V_{out} for each sample was shown in Figure 6. It can be seen that all samples exhibit linear line characteristics. This means that regardless of the annealing temperature it undergoes, ZnO and TiO_2 thin films still acts and operates as a good H^+ sensing membrane.

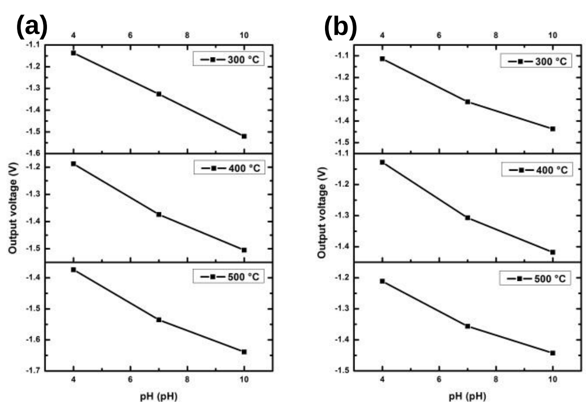


Figure 6 V_{out} for (a) TiO_2 films and (b) ZnO films

Table 1 Sensitivity and linearity values for ZnO samples

Annealing temperature, °C	Zinc oxide	
	Sensitivity, mV/pH	Linearity, %
300	53.80	98.14
400	48.27	98.18
500	38.63	97.98

Table 1 above is the the sensitivity and linearity values displayed by ZnO thin films. All sample has good linearity values ranging from 97.98% until 98.18%. Sample annealed at lowest temperature of 300 °C has the highest sensitivity, in contrast with other samples. When the annealing temperature was being increased, there seems to be a declining in values of the sensitivity of the thin films. This was shown when ZnO annealed at 400 °C has lower sensitivity than 300 °C sample and 500 °C annealed sample demonstrate an even lower sensitivity than the 400 °C sample.

The same trend of decreasing sensitivity exhibit by ZnO thin film was also displayed by TiO_2 thin films. The sample annealed at lowest temperature of 300 °C has highest sensitivity and the value decreased when annealing temperature was increased. Though having the exact same trend, each TiO_2 samples clearly has higher sensitivity values when being compared with its ZnO samples counterparts. This supports our earlier claimed which is TiO_2 has superior sensing performance than ZnO thin films. The overall linearity of TiO_2 samples were also better than ZnO samples (98.44% - 99.99%). Table 2 contains sensitivity and linearity values for TiO_2 sample while Figure 7 are graphical illustration that shows sensitivity pattern demonstrated by both metal oxides when being annealed at different temperature.

Table 2 Sensitivity and linearity values for TiO_2 samples

Annealing temperature, °C	Titanium dioxide	
	Sensitivity, mV/pH	Linearity, %
300	64.00	99.99
400	53.00	99.02
500	44.10	98.44

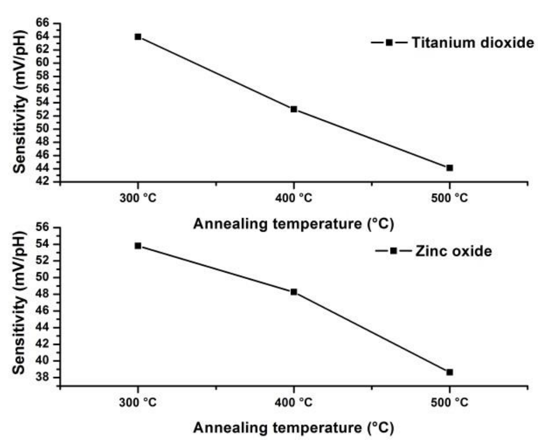


Figure 7 pH sensing trend for TiO_2 and ZnO annealed at different temperature

4.0 CONCLUSIONS

Surface morphology related to roughness of the samples was done. From the AFM images, grain size of ZnO was seen to be slightly larger than grains of TiO_2 thin films. The roughness on surface of TiO_2 thin film was found to be 2.745 nm. ZnO has a much higher surface roughness of 7.792 nm. It is highly probable that the difference in grain size and roughness value between TiO_2 and ZnO was due to the different in aging time of the metal oxide solutions. The metal oxides were incorporated into EGFET pH sensor structure as sensing membrane to detect and measure hydrogen ion concentration in pH buffer solutions.

For detailed comparison purposes, the annealing temperature was varied for both metal oxides. Thin films annealed at 300 °C, 400 °C and 500 °C was prepared and tested for H^+ sensitivity. 300 °C samples has the highest sensitivity and further annealing done above this temperature (400 °C and 500 °C) would results in deteoriation of sensing capabilities. It was found that all TiO_2 sample shows greater sensitivity than ZnO sample at each annealing temperature.

Besides that, the overall linearity observed in TiO2 (98.44% - 99.99%) exceeds the linearity values of ZnO thin films (97.98% - 98.18%). Thus it can be concluded that better sensitivity and linearity value of TiO2 thin film indicates that it was a more suitable material to be used EGFET pH sensor sensing membrane compared to ZnO. However, further studies should be done on structural and electrical properties of both metal oxides thin film to properly explains why TiO2 has greater pH sensing properties than ZnO.

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