Abstract—Sol-gel spin coated titanium dioxide (TiO\textsubscript{2}) was applied as the sensing membrane for extended gate field effect transistor (EGFET) pH sensor. The molarity of the TiO\textsubscript{2} sol-gel was manipulated to study its influence on the film pH sensing capability. In this study, the sol-gel solution concentration was varied from 0.2 M to 1.0 M. It was observed that an increase in molarity used would result in the decrease of pH sensitivity of the TiO\textsubscript{2} thin film, in which, the highest pH sensitivity (42.60 mV/pH) was obtained from the film deposited using the lowest concentration. As sol-gel concentration becomes higher, the films becomes thicker, deteriorating its pH sensing performance. FESEM images showed that the variation of the sol-gel concentration influenced the surface morphology. XRD results obtained confirmed the anatase phase existence in all TiO\textsubscript{2} samples, excluding that of 0.2 M sample that was amorphous with no peaks. Besides that, composite bilayer sensing structure obtained by incorporating ZnO with TiO\textsubscript{2} thin film can produce sensing membrane with higher pH sensitivity than a pure TiO\textsubscript{2} sensing membrane. The sensitivity value for TiO\textsubscript{2}/ZnO and ZnO/TiO\textsubscript{2} composite bilayer samples are 57.1 mV/pH and 46.9 mV/pH respectively.

Index Terms—composite bilayer, EGFET, pH sensor, sol-gel concentration, titanium dioxide

I. INTRODUCTION

PH has been one of the most common electrochemical measurements for its importance in numerous chemical and biological reactions [1]. For a material to be used as pH sensitive membrane, it must possessed several characteristics such as chemically stable [2], does not corrode [3] and non-toxic [4].

More importantly, the material must be able to interact with hydrogen (hydronium) ions in solutions with high sensitivity. Titanium dioxide (TiO\textsubscript{2}) meets those criteria and hence can act as pH sensing membrane.

TiO\textsubscript{2} is a type of metal oxide with three common crystallographic phase; anatase, rutile and brookite [5]. Brookite has orthorhombic crystal system and is the least common [6] compared to both metastable anatase (tetragonal) and thermodynamically stable rutile (tetragonal) [7]. TiO\textsubscript{2} is also an n-type semiconductor with wide band gap [8] between 3.0 eV to (rutile) and 3.2 eV (anatase) [9]. Owing to its unique chemical, physical, optical and electrical properties, TiO\textsubscript{2} had been widely used for various purposes such as sunscreen [10] and pigments [11] and also implemented in many applications like for photocatalysis [12] and sensors [13-14].

A wide variety of methods are available to synthesis TiO\textsubscript{2} thin films. Some examples include but not limited to sputtering [15], chemical vapor deposition [16], spray pyrolysis [17] and sol-gel spin coating [18]. Comparing the methods, sol-gel spin coating is the more desirable deposition technique because of its low deposition temperature, flexibility of material manipulation, relatively lower in cost, excellent final film properties and simplicity in handling.

Solid-state sensing like TiO\textsubscript{2} thin film is more preferable for pH sensing compared to glass-liquid-based pH sensor because of thebrittleness [19], arduous maintenance [20] and miniaturization limitation of the latter [21]. Extended gate field effect transistor (EGFET) sensor structure was introduced in 1983 [22] as alternative to its predecessor ion sensitive field effect transistor (ISFET) [23] and had since been used in pH sensing area [24-25]. In this paper, both TiO\textsubscript{2} and EGFET were integrated with a readout interface circuit (ROIC) to act as a working pH sensor.

There are some other studies reported in literatures discussing capabilities of TiO\textsubscript{2} as membrane for pH sensor with modifications made on the parameters such as annealing temperature [26] and time [27]. However, specific investigation on influence of increasing sol-gel spin coated TiO\textsubscript{2} concentration towards its pH sensitivity using EGFET configuration are scarcely available or almost non-existent.

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Thus this paper concentrates on varying the TiO$_2$ sol-gel molarity to study its effects on pH sensing properties as well as to its physical characteristics.

Another metal oxide that had been used as pH sensing membrane for EGFET pH sensor is zinc oxide, ZnO. Like TiO$_2$, ZnO possessed good chemical stability and can be prepared using similar deposition techniques. Although single layer ZnO and single layer TiO$_2$ had both being used to measure pH of solutions, the combination of both materials in the form of composite bilayer structure as pH sensing membrane is rarely studied. Therefore this work also investigate the influence of integrating TiO$_2$ with ZnO towards its pH sensitivity.

II. EXPERIMENTAL DETAILS

TiO$_2$ sol-gel was produced by mixing different chemicals of different purposes. Titanium (IV) isopropoxide (TTIP) (Ti[OCH(CH$_3$)$_3$]$_4$, Sigma-Aldrich, 97%) as precursor, deionized (DI) water (H$_2$O, Milli-Q Advantage A10) as water source, absolute ethanol (C$_2$H$_5$OH, SYSTEML, 99.8%) as solvent, glacial acetic acid (GAA) (CH$_3$COOH, Friendemann Schmidt, 99.8%) as stabilizer and Triton X-100 (C$_{34}$H$_{62}$O$_{11}$, R&M Chemicals, 98%) as surfactant.

Initially two solutions in two different bottles were made. Solution A contains TTIP (1.5 ml), GAA (2.5 ml) and absolute ethanol (23 ml) while solution B contains Triton X-100 (0.05 ml), DI water (0.2 ml) and absolute ethanol (23 ml). Both solutions were stir at room temperature using magnetic stirrer for one hour before being mixed together. The mixture was then continued to be stirred for one more hour. Then 10 drops of the TiO$_2$ sol-gel was dropped on indium tin oxide (ITO) substrate and spun using spin coating technique. The spinning speed and spinning time during deposition process was 3000 rpm and 60 seconds respectively. After that, the produced TiO$_2$ film was dried at temperature of 200 °C for 10 minutes. To further improve crystallinity of the film, post-deposition annealing process was performed using temperature of 400 °C for duration of 30 minutes.

The steps were repeated but with variation on precursor volume used to produce samples with different concentration of 0.2 M, 0.4 M, 0.6 M, 0.8 M and 1.0 M. To produce composite bilayer samples, a layer of ZnO was added either on top of TiO$_2$ surface (forming TiO$_2$/ZnO composite bilayer film) or at the bottom of the TiO$_2$ layer (forming ZnO/TiO$_2$ bilayer film). The deposition procedure of the ZnO layer was similar to the TiO$_2$ layer but the recipe used to prepare the ZnO sol-gel is different. For ZnO sol-gel, the precursor, zinc acetate was first magnetically stirred with monoethanolamine and 2-methoxyethanol for 3 hours at temperature of 80 °C. Then at room temperature, the stirring process was continued for another 24 hours.

All the fabricated films were then tested for their pH sensing properties by first connecting them to copper wires. Then the copper wires were connected to gate of a metal oxide semiconductor field effect transistor (MOSFET), forming EGFET structure. The MOSFET is a component of a readout interfacing circuit (ROIC) with constant voltage constant current [28]. The ROIC was connected to a multimeter for the output. The overall measurement setup for EGFET pH sensor is illustrated in Fig. 1.

III. RESULTS & DISCUSSION

The fabricated TiO$_2$ thin films were then characterized for its physical properties, namely surface morphology and crystalline quality. Using field emission scanning electron microscopy (FESEM), the surface morphology images were obtained and shown in Fig. 2.

![Fig. 1. Schematic diagram of pH measurement setup of EGFET pH sensor](image-url)
For the TiO$_2$ film fabricated using lowest sol-gel concentration of 0.2 M, the TiO$_2$ was uniformly distributed throughout the film but there are no significant structural growth can be clearly seen. However, upon closer observation using bigger magnification of x50,000, there are several small, randomly shaped particles (marked by the circles). At higher concentration of 0.4 M, the particles that was previously seen in 0.2 M sample seems to have grown into larger particles and are connected with each other, forming branching networks of TiO$_2$ structure. 0.6 M sample exhibits a more distinct structural growth. It is a structure formed from countless of irregularly rounded or spheroid particles bonded to each other. Besides that, the growth of TiO$_2$ particles for 0.6 M sample clearly happens both horizontally and vertically, unlike the previous sample. The shape is comparable to reported work that used TiO$_2$ nanopowder in the sol-gel processing [29].

The sample being prepared using solution of 0.8 M concentration is presented in Fig. 2d. The structure of the sample is completely different from the lower concentration samples where the particles might have completely merged with each other as a result of the high concentration used, forming a dense TiO$_2$ film. The film has smooth-surface film with cracks existing at many places. The high precursor concentration might had caused additional stress on the films during annealing steps, creating the macroscopic cracks [30]. The same can be said for the subsequent sample of 1.0 M but with one major difference. The cracks that existed is far bigger and these cracks separate dense TiO$_2$ blocks from one another.

The crystalline quality of the TiO$_2$ samples were determined using X-ray diffraction (XRD) technique and the results are shown in Fig. 3. For 0.2 M sample, no peaks appeared, indicating it is not crystalline and thus amorphous [31]. This amorphous nature of the first sample means its atoms has no long-range order of preferred atomic arrangement. As the concentration being raised to 0.4 M, several distinctive peaks emerged. There is one major peak at 2-theta (20) of 25° and five minor peaks at 38°, 48°, 54°, 55° and 63°. These peaks correspond to Miller indices of (101), (112), (200), (105), (211) and (204) respectively.

Based on available literature [32] and standard card JCPDS 00-021-1272, these peaks confirms that the produced 0.4 M sample contains anatase phase. The common reported crystal arrangement for TiO$_2$ are tetragonal (anatase and rutile) [33]. However, the reason for anatase to become dominant in this sample might be due to the low annealing temperature applied in this study which is 400 °C. Rutile on the other hand can only be obtained using high temperature treatment (800 °C-1000 °C) [34-35]. Besides, synthesis of TiO$_2$ generally formed anatase as the initial crystalline phase and this is caused by two factors. First is the tendency of short-ranged order Ti$_6$ to arranged into long-range ordered anatase structure and second is due to the thermodynamic characteristics of both anatase and rutile may had favored crystallization of anatase [36]. When concentration of sol-gel being further increased to 0.6 M, the same pattern of peaks is also observed for the sample. The same can be said for the subsequent samples of 0.8 M and 1.0 M but the major peak of these two samples shows a slight increment in the intensity value.

The TiO$_2$ thin films were then characterized for their pH sensitivity and linearity to determine its sensing performance. Since TiO$_2$ is a metal oxide, it has hydroxyl (OH) [37] groups that can interact with acidic and basic solutions, displaying amphoteric behavior [38]. This means that TiO$_2$ is capable of interacting with both hydrogen and hydroxide ions in solutions [39]. When TiO$_2$ films were used as pH sensing membrane, the output voltage of EGFET pH sensor would differs depending on acidity and basicity of solutions being measured. The graph of output voltage, $V_{out}$ vs pH recorded for all samples are plotted in Fig. 4.
All the lines in graph in Fig. 4 is almost linear, suggesting good correlation between the two variables. Different $V_{out}$ was produced by sensing membrane when being measured in different pH buffer solution. The reason behind it is that the amount of pH potential determining ions (H$^+$ and OH$^-$) vary according to the solution’s pH value and this affect surface potential, $\Psi_0$ produced at the surface of sensing membrane. According to site binding theory based on Gouy-Chapman-Stern Model \[40\], the relationship and dependency of $\Psi_0$ with solution’s pH value can be expressed using equation (1) \[41\]:

$$2.303 \left( p_{H_{pzc}} - pH \right) = \frac{q\Psi_0}{kT} + \sinh^{-1}\left(\frac{q\Psi_0}{kT}.\frac{1}{\beta}\right)$$  \(1\)

Where $p_{H_{pzc}}$, q, k, T and $\beta$ are pH at point of zero charge, electron charge, Boltzmann’s constant, absolute temperature and sensitivity parameter respectively. The output voltage, $V_{out}$ was seen to become more negative as pH value becomes higher. One possible explanation is that as pH value rises, amount of OH$^-$ increases, producing negative surface potential, $\Psi_0$ at TiO$_2$-solution interface. As a result, $I_{DS}$ in MOSFET is reduced \[42\] and thus this lead to decreased in $V_{out}$ values. In contrast, the higher $V_{out}$ achieved by more acidic solution might due to presence of many H$^+$ (hence positive $\Psi_0$) on the surface of TiO$_2$ sensing membrane.

The pH sensitivity and linearity value for each TiO$_2$ sample was extracted from the slope of the graphs in Fig. 4, and shown in Fig. 5. The sensitivity of the first sample (0.2 M) is 42.6 mV/pH with linearity of 0.9497. The second sample (0.4 M) possessed slightly lower sensitivity of 41.7 mV/pH and its linearity is 0.9853. This declining pH sensitivity trend continues with all the subsequent TiO$_2$ samples. TiO$_2$ thin films with 0.6 M, 0.8 M and 1.0 M have sensing performance of 40.1 mV/pH (0.9615), 39.0 mV/pH (0.9692) and 25.1 mV/pH (0.8213) respectively.

The declining sensitivity pattern can be seen in Fig. 5. The TiO$_2$ film’s sol-gel concentration and its pH sensitivity having inversely proportional relationship can probably be attributed to the increment of the film’s thickness as reported by other researchers. The investigation from work done by Stephen Lourduraj et al., \[43\] reported that as molarity of sol-gel increases, the resultant film thickness also increased. While Pin Chuan Yao et al., \[27\] reported that thicker film has lower sensitivity. However, the films thicknesses in our work are shown in Fig. 6 below. The error bar showing the highest and lowest values are also incorporated with the marker showing the average thickness value. The measurements were done using the surface profiler by taking a few points on the same sample. It can be seen that in average, the thickness increases with the molarity, however, at higher molarity, it can be observed that the uniformity of the thin film is not as good as those of the lower molarity. This may be related to the viscosity of the solution; higher viscosity solution has a higher tendency to produce a thin film with non-uniform thickness compared to those with lower viscosity. Thus, relating the sensor results in Fig. 5 to the thicknesses in Fig. 6, we may not be able to correlate the film thickness and uniformity to the sensor performance. The performance pattern seen in Fig. 6 may be attributed to various factors such as surface morphology and crystalline quality, which need to be studied further.
While there are many reports on the single material sensing layer and sensing membrane made up of doped materials, only limited number of reports found for pH sensing layer using more than one material in the form of composite bilayer structure. Hence in an attempt on increasing the sensitivity, TiO$_2$-based composite bilayer structure were fabricated. This is because the highest pH sensitivity obtained above is still far from the Nernstian theoretical value of 59 mV/pH. In this bilayer configuration, a layer of ZnO is added on top of (TiO$_2$/ZnO) or at the bottom of TiO$_2$ layer (ZnO/TiO$_2$).

The results from examination of surface of TiO$_2$/ZnO and ZnO/TiO$_2$ samples are shown in Fig. 7. For TiO$_2$/ZnO sample, the structure is similar to structural formation in Fig. 2 (b) while ZnO/TiO$_2$ is made up of numerous nanocrystallites [44] that is almost densely packed together. The structural differences between both films resulted in different roughness on the surface. From From the AFM images in Fig. 8, the surface roughness for TiO$_2$/ZnO and ZnO/TiO$_2$ are 2.228 nm and 1.266 nm respectively. 

![Fig. 6. TiO$_2$ thin film thickness dependence on the molarity](image)

![Fig. 7. Surface structure on (a) TiO$_2$/ZnO and (b) ZnO/TiO$_2$ composite bilayer samples](image)

![Fig. 8. AFM images for (a) TiO$_2$/ZnO and (b) ZnO/TiO$_2$ sample](image)

To determine the sensitivity of both composite bilayer samples, V$_{out}$ vs pH graph is plotted as in Fig. 9. In term of sensitivity, there is an increment for ZnO/TiO$_2$ composite bilayer sample (46.9 mV/pH) compared to single layer TiO$_2$ sample (42.6 mV/pH). On the other hand, the sensitivity was significantly enhanced when TiO$_2$/ZnO composite bilayer configuration was used. The pH sensitivity for this sample is 57.1 mV/pH and thus approaching the Nernst theoretical value of 59 mV/pH. The sensitivity improvement caused by the usage of composite bilayer configuration is yet to be determined. However, it is clear that the synergetic effects arising from the combination of the two materials used can be beneficial in producing high performance pH sensing membrane.

![Fig. 9. pH sensitivity and linearity for the composite bilayer samples](image)
IV. CONCLUSION

The results presented in this study showed that fabricated sol-gel spin coated TiO$_2$ thin films are capable of acting as pH sensing membrane, with the highest sensitivity achieved was 42.6 mV/pH. The properties of the films were found to be dependent on concentration of precursor used. By increasing molarity of TiO$_2$ sol-gel solution, the pH sensing performance of TiO$_2$ sensing membrane were observed to experience deterioration, as shown by declining sensitivity values. The surface structure of TiO$_2$ films also changes when molarity being changed with 0.6 M sample exhibit nanostructure growth. In term of crystalline quality, although amorphous characteristics displayed by 0.2 M sample, all other TiO$_2$ samples with higher concentration demonstrated high degree of crystallinity. It was also found that the sensitivity of the sample can be improved when TiO$_2$ film was combined with ZnO film and thus forming composite bilayer structure. The TiO$_2$/ZnO has pH sensitivity of 57.1 mV/pH while ZnO/TiO$_2$ sample has pH sensitivity of 46.9 mV/pH.

REFERENCES


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