Jurnal Teknologi

Full Paper

EVALUATION ON THE EGFET PH SENSING PERFORMANCE OF SOL-GEL SPIN COATED TITANIUM DIOXIDE THIN FILM

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Article history
Received
17 November 2020
Received in revised form
7 April 2021
Accepted
19 May 2021
Published online
20 June 2021

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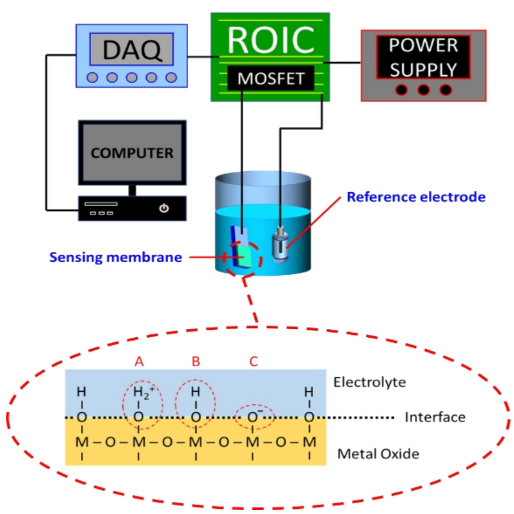
Graphical abstract



Abstract

For this study, TiO_2 thin film was fabricated using sol-gel spin coating method. The fabricated film was then applied as sensing membrane in an extended gate field effect transistor (EGFET) pH sensor system. The pH sensing performance of the sol-gel spin coated TiO_2 were evaluated in terms of sensitivity, linearity and hysteresis where the value obtained was 58.70 mV/pH, 0.9922 and 86.17 mV respectively. The drift rate of the sample when being measured for 12 consecutive hours was also determined where measurement in pH 4, pH 7 and pH 10 yield drift rate of 1.72 mV/h, 4.14 mV/h and 6.05 mV/h respectively. Besides that, the TiO_2 was characterized for its thickness (24.32 nm) and surface roughness (5.129 nm). From the results obtained, it was found that sol-gel spin coated TiO_2 thin film with thickness between 20 - 29 nm will have high pH sensitivity (more than 50 mV/pH).

Keywords: EGFET, pH sensors, sol-gel spin coating, thickness, thin films, titanium dioxide

Abstrak

Untuk kajian ini, filem nipis TiO_2 telah difabrikasi menggunakan kaedah salutan putaran sol-gel. Filem yang telah difabrikasi kemudian digunakan sebagai membran pengesan di dalam sistem sensor pH 'extended gate field effect transistor'. Prestasi pengesanan pH oleh TiO_2 salutan putaran sol-gel telah dinilai dari segi kepekaan, linearity dan hysteresis di mana nilai yang diperoleh masing-masing adalah 58.70 mV/pH, 0.9922 dan 86.17 mV. Kadar drift sampel ketika diukur selama 12 jam berturut-turut juga telah ditentukan di mana pengukuran dalam pH 4, pH 7 dan pH 10 menghasilkan kadar drift masing-masing adalah 1.72 mV/h, 4.14 mV/h dan 6.05 mV/h. Selain itu, TiO_2 juga dicirikan untuk ketebalannya (24.32 nm) dan kekasaran permukaan (5.129 nm). Dari keputusan yang diperoleh, telah didapati bahawa filem nipis TiO_2 salutan putaran sol-gel dengan ketebalan antara 20 – 29 nm akan mempunyai kepekaan pH yang tinggi (lebih dari 50 mV/pH).

Kata kunci: EGFET, sensor pH, salutan putaran sol-gel, ketebalan, filem nipis, titanium dioxide

1.0 INTRODUCTION

pH measurement is vital for various purposes. Agriculture area [1], construction sector, medical field [2-3] and food processing [4] all are pH dependent. Cheap litmus paper is extremely good for acid, neutral and basic solution differentiation but unsuitable when precise measurement is needed. Glass pH electrode is popular since it gives accurate pH measurement but suffers drawbacks of mechanical fragility making it unfit to be used in some applications especially in in-vivo measurement [5]. To solve this, Bergveld [6] introduced an alternative pH sensing structure known as ion sensitive field effect transistor (ISFET). Based on MOSFET operating principle, ISFET showed promising performance with pH sensitivity more than 50 mV/pH.

The only problem arose was that the MOSFET used was being immersed along with pH sensitive part during the measurement process. This makes ISFET somewhat unreliable when dealing with temperature and light as well as having issues of ionic penetration. A simple yet effective solution was proposed by Spiegel et. al [7] to eliminate the problem faced by ISFET. By extending the gate from the MOSFET, the sensing membrane now no longer needed to be fabricated directly on MOSFET. Thus the MOSFET does not need to be immersed in solutions being measured. This extended structure is considered as successor to ISFET and known as extended gate field effect transistor (EGFET). EGFET pH sensing structure offers significant advantages such as light and thermal stability, simpler packaging and dimensional flexibility of the sensing membrane [8].

Common method of measuring pH is by using glass electrode because of its sensitivity. However, since it is glass-built nature, the glass electrode is large in size, difficult to be miniaturized and mechanically fragile [9]. Besides that, glass electrode used for pH measurement needs internal solution, complicating its fabrication process. It also requires high maintenance since need to be immersed in a specialized solution when not being in used and periodically calibrated [10]. All solid-state sensing membrane is therefore more favored compared to glass pH electrode. Some of sensing membrane type popularly used is metal nitride based and metal oxide based. These groups of material have special properties on its surface, enabling it to interact with hydrogen ions in liquid solutions.

In case of metal oxide, it has surface hydroxyl groups which can protonate and deprotonate at moment of contact with hydrogen ions in solutions, producing surface potential [11]. When being used as sensing membrane for EGFET pH sensor, the surface potential at metal oxide-electrolyte interface would change the amount of current that can flow between source and drain in the MOSFET used. The amount of current is dependent on amount of hydrogen ions available in measured solution and these would affect the output voltage, V_{out} reading of EGFET pH sensor. Based on output voltage obtained, the pH values of solutions can be determined, and vice versa.

The performance of metal oxide as pH sensing membrane however is highly associated with its fabrication process. Metal oxide such as titanium dioxide can be produced through many deposition methods such as chemical vapor deposition, sputtering, dip coating, spin coating, spray pyrolysis and pulsed laser deposition [12]. Comparing all of the techniques, sol-gel spin coating is considered the most compelling film forming method because of its simplicity, low cost, low temperature deposition and final product properties [13].

There are several characterizations that can be done to study the sensing performance of a thin film when measuring pH. In this work, the pH sensitivity, linearity, hysteresis and drift characteristics of the fabricated TiO_2 thin film was measured and determined. Besides that, a range of ideal thickness for a sol-gel spin coated based TiO_2 pH sensing membrane was proposed in this work.

2.0 METHODOLOGY

Ultrasonic cleaning of electrically conductive indium tin oxide (ITO) substrate was performed using Hwashin Technology Powersonic 405 ultrasonic cleaner. The cleaning solution used was methanol and deionized water. Inert argon gas was then used to blow-dry the cleaned substrate.

The sol-gel used was 0.1 M TiO_2 solution. The sol-gel was obtained by mixing titanium (IV) isopropoxide (Sigma-Aldrich, 97%) precursor with deionized water (Milli-Q Advantage A10) for it to undergo hydrolysis process. The solvent, stabilizer and surfactant used was absolute ethanol (SYSTERM, 99.8%), glacial acetic acid (Friendemann Schmidt, 99.8%) and Triton X-100 (R&M Chemicals, 98%) respectively. The mixture was stirred for 2 hours using Stuart Digital Hotplate Stirrer CD162 to obtain homogenous and clear solution.

To deposit TiO_2 in form of thin film, spin coater (Laurell Model WS-650MZ-8NPP/LITE) was used. The process was started by positioning cleaned ITO substrate on top of the spin coater's chuck. Then, 10 drops of prepared TiO_2 sol-gel was dropped on top of the substrate. The speed of the substrate being rotated during the sol-gel deposition was 500 rpm. After the deposition was done, the rotational speed of the substrate was increased to 3000 rpm for 1 minutes. During this high-speed spinning, the deposited solution would be uniformly distributed across substrate surface by the action of centrifugal force.

After spinning process had finished, the substrate was removed from the spin coater's chuck. To remove the excess solvent from the film, drying process was conducted at temperature of 100 °C for 10 minutes and the film was then subsequently annealed for 15 minutes at 400 °C to remove any organic residues. All the heat treatment was performed using Protherm Furnace PLF 160/5.

The dried and annealed TiO_2 thin film was used as sensing membrane for EGFET pH sensor. This was done by connecting it to the gate of a commercialized MOSFET using copper wire, forming the EGFET configuration. The MOSFET was attached to a constant voltage constant current (CVCC) readout interface circuit (ROIC) [14]. The output voltage, V_{out} from the ROIC was recorded by Keysight U2356A 64CH Multifunction data acquisition (DAQ). The setup used was shown in Figure 1.

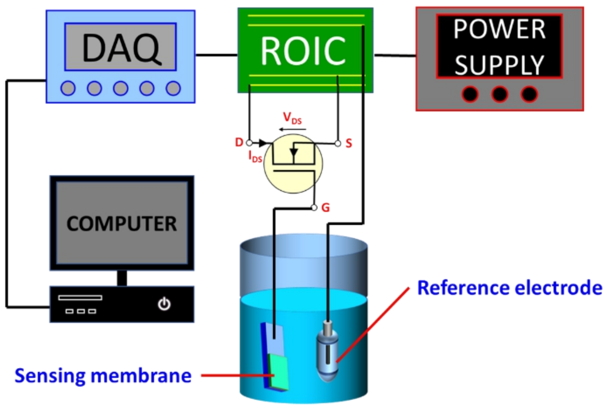


Figure 1 EGFET pH measurement setup

3.0 RESULTS AND DISCUSSION

Using surface profilometer, thickness of the TiO_2 thin film was measured and was found to be at 24.32 nm. The surface of the sample was scanned using atomic force microscope (AFM) and the resulting image was shown in Figure 2. The average roughness, R_a of the surface of the sample was 5.129 nm. Besides that, EDX characterization was performed. The peaks representing elements present on the sample was shown in Figure 3 with Ti and O confirmed to be existed. Besides that, peak of elements from the substrate namely Si, In and Sn was also observed.

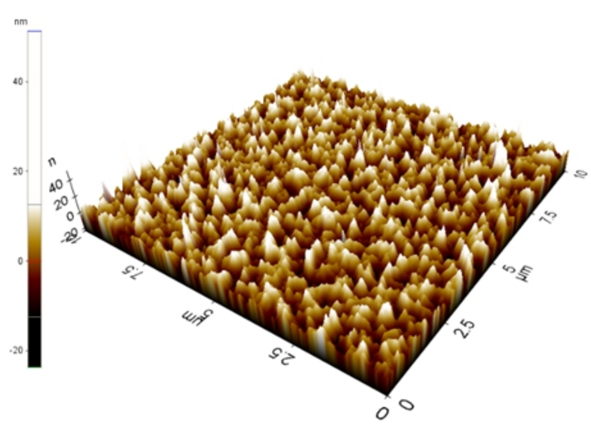


Figure 2 AFM 3D image showing surface morphology of the spin coated TiO_2 thin film

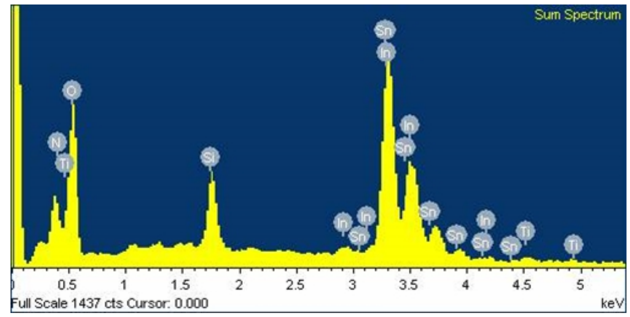


Figure 3 EDX spectra of the TiO_2 thin film

For pH sensor, the most important characteristic is that it must possessed good sensitivity. Sensitivity is a measurement in which the sensitive layer, here the TiO_2 thin film, was evaluated for its ability to interact with hydrogen ions in the solution. Higher sensitivity value means better sensing performance and ideal sensitivity was derived from Nernst equation, shown in Equation 1 [15].

$$E = E^{\circ} - \frac{0.0592\,V}{n}\log Q \qquad (1)$$

in which E, E°, n and Q are cell potential, standard cell potential, number of electrons and reaction quotient respectively. From the equation, the ideal sensitivity that was desired is 0.0592 V or 59.2 mV. In pH sensor term, this value means that for every change of 1 pH value of solution, the voltage produced has 59.2 mV differences. In an EGFET sensor system, since the sensitivity was directly extracted from the slope of the graph of output voltage versus pH value, the output voltage is considered an important aspect of the measurement. To understand how output voltage was obtained using EGFET system, pH sensing mechanism and MOSFET working principle must be understood. TiO_2 was chosen as the sensing membrane since as a metal oxide, its surface has hydroxyl groups [16-17]. These hydroxyl groups were capable of interacting with pH potential determining ions (PDI) that is hydrogen ions and hydroxide ions.

When a PDI comes into contact with the hydroxyl group, the hydroxyl group will either protonate (donate electron) or deprotonate (accept electron) [18], shown in the Figure 4. Thus depending on the type of PDI that is dominant in the solution (hydrogen ions in acidic solution while hydroxide ions in basic solution), the surface of the sensing membrane will be either be more positively or more negatively charged. This is measured in term of surface potential following the Equation 2 below:

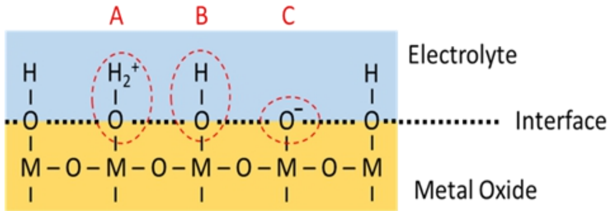


Figure 4 Basic reaction on metal oxide surface producing surface potential (a) protonation (b) neutral condition (c) deprotonation

$$2.303(pH_{pzc} - pH) = \frac{q\Psi_0}{kT} + sinh^{-1}(\frac{q\Psi_0}{kT}.\frac{1}{\beta}) \qquad (2)$$

where pH_{pzc} is pH value at point of zero charge, q is electron charge, Ψ_0 is the surface potential, k is Boltzmann's constant, T is absolute temperature and β is the sensitivity parameter. The surface potential would determine the amount of current that may flow between the source and drain (I_{DS}) in the MOSFET. The I_{DS} would then influence the resultant output voltage and hence the sensitivity value of the sample. In short, the output voltage is dependent on the amount or concentration of PDI available in the solution.

Graph correlating output voltage and pH value was plotted as in Figure 5. The sensitivity and linearity value of the sample was extracted from the slope and regression value of the graph respectively. As a result, the pH sensitivity of the sample was found to be at 58.70 mV/pH while its linearity was 0.9922. This value is considered high and also obey the Nernstian theoretical response of 59 mV/pH [19].

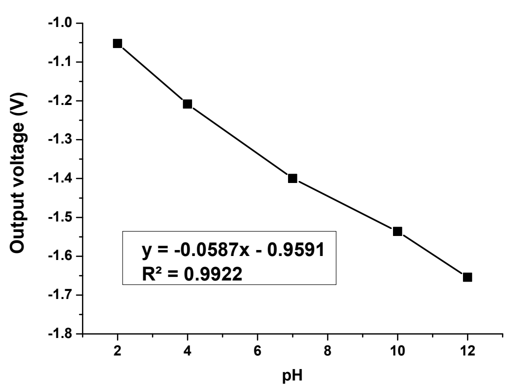


Figure 5 Output voltage vs pH value

In a metal oxide-based pH sensing membrane, another sensing performance evaluation that was usually studied is the hysteresis measurement. Hysteresis effects refers to the changes in reading after the sample being measured in pH buffer solutions of different value. It involves measuring the output voltage of sample when being immersed in a loop of pH buffer in a given time. There are generally two kind of hysteresis measurement can be done; acid-site or basic-site. For example, in an acid-site measurement, the pH loop is 7-4-7-10-7 while for basic-site, the pH loop is 7-10-7-4-7.

It basically means either the measurement starts (after being immersed in pH 7) with measurement in acidic media or basic media. In this particular study, acid-site hysteresis measurement was performed. The pH loop is 7-4-7-10-7 in a period of 600 seconds. The graph of the result from the hysteresis measurement is shown in Figure 6 below. The hysteresis of the sample was determined by measuring the difference of output voltage between initial and final reading (ΔV_{out}) during the hysteresis measurement.

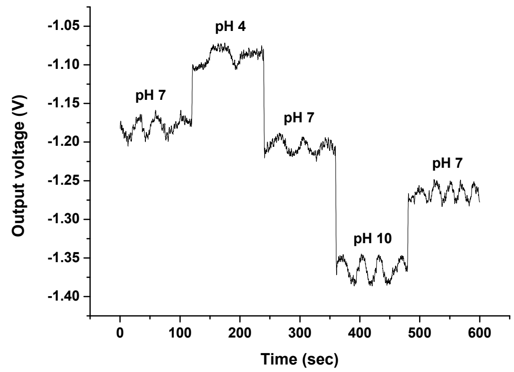


Figure 6 Hysteresis characteristics of spin coated TiO_2 EGFET pH sensor

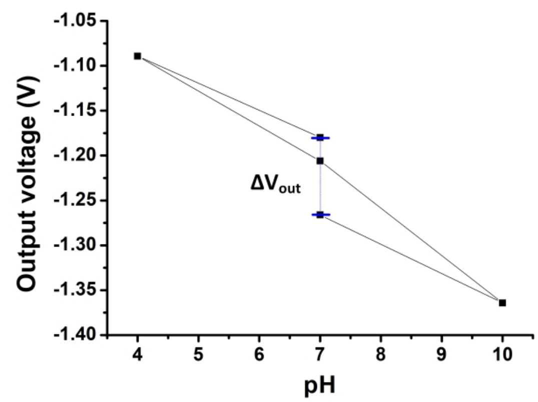


Figure 7 Hysteresis width of the spin coated TiO_2 EGFET pH sensor

The ΔV_{out} can also be called hysteresis width, H_w and in this work, the H_w for the TiO_2 thin film is 86.17 mV (shown in Figure 7). Hysteresis is also known as memory effect where this abnormality is caused by presence of buried OH site beneath the surface of inorganic pH sensitive membrane [20]. Number of buried sites is expected to be lower than available on surface, but H^+ and OH^- ions can diffuse slowly into the surface [21]. This very slow response resulted in apparent delay or hysteresis effects experienced by the sensing membrane [22].

The reliability of the sensing membrane is further investigated in which the sensing performance of the TiO_2 film is studied for an extended period of time. This was done to study the drift characteristic of the fabricated sample. Drift is a phenomenon [23] in which the value of reading changes over time when being measured in a fixed value of pH buffer solution. In this work, the TiO_2 sensing membrane was immersed in the same pH buffer solution (pH 4, 7 and 10) for 12 consecutive hours. The V_{out} produced were recorded by the DAQ and was plotted in the graph in Figure 8.

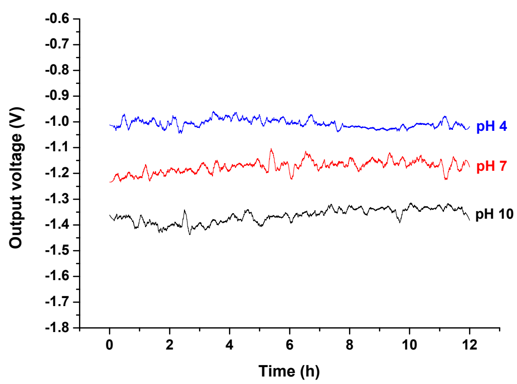


Figure 8 Drift characteristics of the spin coated TiO_2 thin film pH sensor measured for 12 consecutive hours

The drift of the sensing membrane when being measured in pH 4 buffer solution is quite small with drift rate of only 1.72 millivolt per hour (mV/h). When solution with pH value of 7 was used, the drift rate increases to 4.14 mV/h. Highest drift rate of 6.05 mV/h was observed when the measurement was done in buffer solution of pH 10.

From the result, it was noticed that drift values become larger as solution's pH value increases. The dependent of drift on pH value could be related to the amount of potential determining ions, H^+ and OH^- present. Higher pH means higher numbers of OH^-. This means that the increase in drift was influenced by higher amount of OH^- in the solutions [24]. This phenomenon on drift-pH increment is also observed in other type of pH sensitive materials [25-26].

Deviation of output voltage as a result of prolong measurement is an issue commonly occurred in metal oxide based ISFET pH sensor. EGFET, a successor to ISFET sensor structure also possessed this long-term drift effects, as shown in this study. It is suggested that drift may be caused by several possibilities; variation of the surface state density, slow surface effects, drift of sodium ions or by injection of electrons from the electrolyte [20].

Sol-gel spin coating process was also used to fabricate TiO_2 thin films while varying other parameters, resulting in films with different thickness. The film's thickness seems to affect the pH sensitivity of the samples when being used as sensing membrane for EGFET pH sensor structure, as shown in Figure 9.

From Figure 9, the increase in film thickness seems to improve the pH sensitivity of TiO_2. Increase in film thickness in the same fixed area, can be related to the increase of TiO_2 particles in the volume element of the thin films as it becomes thicker. We take into account the region that involves in the pH sensing mechanism which is the surface and the region below the surface, more TiO_2 particles in the region means more oxygen atoms concentration per unit area. The thickness of this region and the concentration of the oxygen atoms were reported to be among the determining factor of the surface hydroxyl groups concentration [27]. With the increase of TiO_2 particles concentrations, more hydroxyl groups become available on the surface of the film to enhance more interaction with PDIs and thus improve the sensitivity. However, based on [27], the determining factors are based on the region below the surface area and not the bulk of the thin film. Hence further increasing the film thickness will not improve the sensor sensitivity. Thicker films were also reported to be less sensitive than thinner films due to the formation of internal potential difference between the thin film surface and the substrate [28]. This affects the flow of current to the MOSFET and thus may lowered the sensitivity of the sensor.

It was also noticed in Figure 9 that in order for a TiO_2 thin film to possessed great pH sensitivity above 50 mV/pH (data in circle), the film thickness must be between 20 nm-29 nm range. Most of the sample that has thickness lower and higher that this range would most probably has sensitivity lower than 50 mV/pH. Although sensitivity above 40 mV/pH is still consider good, for usage in important applications that require high precision pH measurement, a high sensitivity sensing membrane near Nernstian value (59 mV/pH) is needed. But it is noteworthy to note that this range of thickness was obtained using TiO_2 sample with sol-gel concentration of 0.1 M and might differs if different concentration is used.

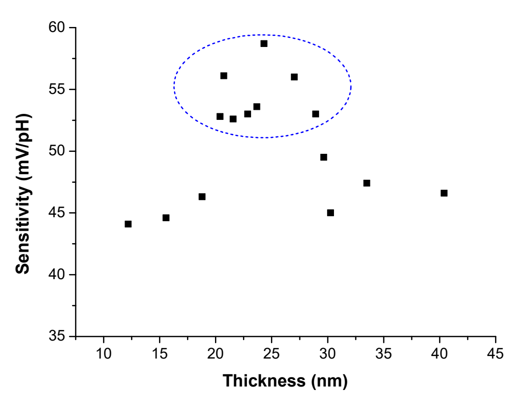


Figure 9 pH sensitivity dependency on thickness of sol-gel spin coated TiO_2 thin films

4.0 CONCLUSION

Sol-gel spin coating method was used to fabricate pH sensitive TiO_2 thin film. The thickness of the produced film was found to be at 24.32 nm while the surface roughness is 5.129 nm. Using EGFET sensor measurement setup, the film pH sensing characteristics were determined through measurement of sensitivity (58.70 mV/pH), linearity (0.9922), hysteresis (86.17 mV) and drift (4.14 mV/h at pH 7). A range of sol-gel spin coated TiO_2 film thickness that can result in highly pH sensitive film (more than 50 mV/pH) was also successfully determined in this work. The thickness range was found to be at 20 nm to 29 nm.

Acknowledgement

This study was partially supported by MOSTI Malaysia under the International Collaboration Fund (ICF) (Grant number: IF1019/1136). Authors acknowledge the technical support from NANO-SciTech Centre (NST), UiTM.

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