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pH SENSITIVITY DEPENDENCY ON THE ANNEALING TEMPERATURE OF SPIN-COATED TITANIUM DIOXIDE THIN FILMS

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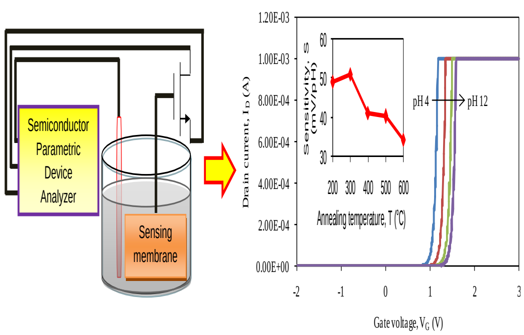
Graphical abstract



Abstract

Titanium dioxide (TiO_2) thin films were fabricated on indium tin oxide (ITO) glass substrates using the spin coating technique and further were implemented as sensing membranes of the extended gate field effect transistor (EGFET) based pH sensor. The as-deposited thin films were annealed at different temperatures from 200 - 600 °C in room ambient for 20 min. The effects of different annealing temperatures on electrical and crystalline properties were analyzed by *I-V* two point probes measurement and X-ray diffraction respectively. Meanwhile, the surface morphology of thin films was observed by field emission scanning electron microscope (FESEM). We then measured the transfer characteristics (I_D-V_G) of the TiO_2/ITO sensing membrane using a semiconductor parametric device analyzer for sensor characterization. It was found that, TiO_2/ITO sensing membrane annealed at 300 °C achieved higher sensitivity and good linearity of 51.48 mV/pH and 0.99415, respectively in the pH buffer solutions of 4, 7, 10, and 12. Thin film annealed at 300 °C gives higher conductivity thin film of 384.62 S/m. We found that the conductivity of TiO_2/ITO thin films was proportional with the sensitivity of sensing membrane.

Keywords: Annealing temperature; extended gate field effect transistor; sol-gel spin coating; titanium dioxide

1.0 INTRODUCTION

pH is a measure of hydrogen (H^+) ion concentration in a solution and is important in numerous field of applications such as in medical and biomedical analysis, agriculture and aquaculture, environment monitoring, and food processing technology [1-4]. There are some commonly used tools for pH measuring like litmus paper and pH glass electrode because of simple and quick measurement result [5]. Nevertheless, there are some drawbacks regarding these two tools. Example, pH glass electrode is fragile, temperature dependant and requires frequent monitoring maintenance [6]. Incorporating silicon technology with sensors has been started since 1970 and among the most well-known example is the ion sensitive field effect transistor (ISFET) introduced by Bergveld [7]. ISFET was developed from modifying the metal oxide semiconductor field effect transistor (MOSFET) for an alternative way for previous problems. However, ISFET still have some problems, including unstable and costly. Next, Van der Spiegel et al [8] employed the same principle as ISFET to build extended gate field effect transistor (EGFET). EGFET is composed of isolated FET connected with sensing membrane where only the sensing membrane is exposed directly to the electrolyte. Thus, this configuration offers more benefits such as simple and easy in packaging, low cost, light and temperature insensitivity, etc. In addition, the structure of EGFET is suitable as disposable sensor due to the reusable separate MOSFET while the sensing membrane is exchanged.

Previously, the first invented metal oxide layer used as sensing membrane was silicon dioxide (SiO_2) [7]. However, due to low sensitivity and large drift other metal oxide layer been explored as an alternative sensing membrane layer such as aluminum oxide (Al_2O_3) [9], tin oxide (SnO_2) [10], tantalum pentoxide (Ta_2O_5) [11], and titanium dioxide (TiO_2) [12] because of the ability to sense H+ ion. Among those materials, TiO_2 is a n-type semiconductor and have its own advantages like inexpensive, chemically stable, and non-toxic material [13] and thus, is chosen as the sensing material in this work.

In this paper, we present the study of the annealing temperature effect on TiO_2 sensing membrane for EGFET pH-sensing application. The electrical, physical and crystalline properties dependences on the annealing temperature of the TiO_2 thin films were studied. Then, the EGFET sensor was characterized for its transfer characteristics to analyze the sensitivity of TiO_2/ITO thin films.

2.0 EXPERIMENTAL

2.1 Solution Preparation

The TiO_2 solution was made by mixing two solutions which were labeled as solution A and solution B. Solution A contained three types of chemicals that is absolute ethanol ($C_2H_5OH_5$), glacial acetic acid; GAA (CH_3COOH) and titanium isopropoxide; TTIP ($Ti(OCH(CH_3)_2)_4$. Meanwhile, for solution B consisted of absolute ethanol ($C_2H_5OH_5$), triton x-100 $C_{14}H_{22}O$ (C_2H_4O) n(n=9-10) and deionized water. Both solutions A and B were mixed and stirred in a separate bottle at a speed of 2000 rpm for 60 min. Next 60 min, both solutions A and B were mixed together in one bottle for another 60 min at speed of 2000 rpm at room temperature.

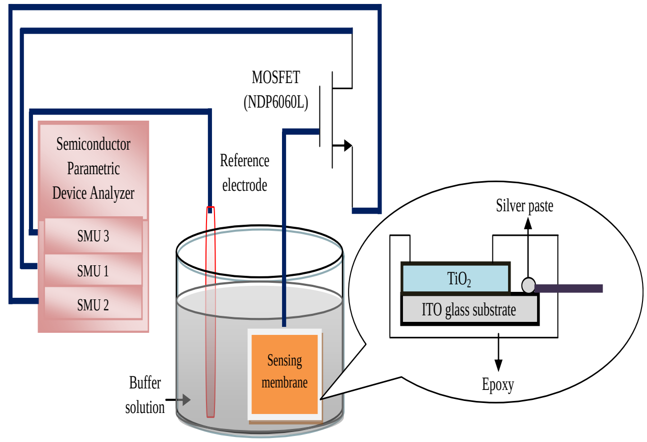


Figure 1 Measurement setup of EGFET pH sensor

2.2 Thin Film Deposition

The TiO_2 thin film was deposited on ITO coated glass substrate. The ITO glass substrates were cleaned by the standard organic cleaning prior to the thin film deposition. We choose ITO coated glass as a substrate to deposit TiO_2 thin films because the conductive layer of ITO can be the conductor to be connected to the gate of transistor (NDP6060L). The rotation speed and spinning time of spin coater was set to 3000 rpm and 60 second accordingly. Then, the TiO_2 solution was deposited onto an ITO coated glass and were annealed at 200 – 600 °C for 20 min each. Electrical and surface morphology of thin films was investigated by *I-V* two point probe measurements (BUKOH KEIKI-EP2000) and field emission scanning electron microscope, FESEM (JEOL-JSM 7600F). Meanwhile, X-ray diffractometer, XRD (Rigaku Ultima IV with a Cu Kα), in which λ = 0.15406 nm, was used to analyze the crystalline properties of thin films.

2.3 Measurement Setup of EGFET pH Sensor

The fabricated TiO_2/ITO sample was connected to metal wire with silver paste to form the sensing membrane. To prevent the leakage current from occurring during measurement, all thin films was encapsulated with epoxy resin. The exposure region for opening window of sensing membrane was defined as 1 cm x 1 cm for each thin film to eliminate the effect of sensing area to the sensor sensitivity.

The encapsulated sensing membrane was connected to the gate of commercial metal oxide semiconductor field effect transistor, MOSFET device (NDP6060L). Semiconductor parametric device analyzer model Agilent B1500A was used to measure the transfer characteristic (*I-V*) and sensing performance of deposited thin films. TiO_2/ITO deposited thin film and the reference electrode (Ag/AgCl) were dipped in various value pH buffer solutions of pH 4, 7, 10 and 12 in a dark box to prevent from temperature and light influences. The use of reference electrode (Ag/AgCl) is to ensure the proper operation and constant voltage during the measurement process. Figure 1 shows the measurement setup system for EGFET.

3.0 RESULTS AND DISCUSSION

3.1 Electrical Properties of TiO_2 Thin Films

Figure 2 shows the current-voltage (*I-V*) characteristics of Au/TiO_2/ITO thin films annealed at various temperatures of 200 – 600 °C for 20 min. The voltage was swept from -10 to 10 V. Gold (Au) was deposited as metal contact onto the TiO_2 films because of a standard metal contact and stable low resistance material properties. From the graph, it can be seen that increases in voltage resulted in the increase of current which shows that the ohmic contact was formed. The graph shows that the least resistive thin film are 300 °C followed with 200 °C, 400 °C, 500 °C and the most resistive is 600 °C.

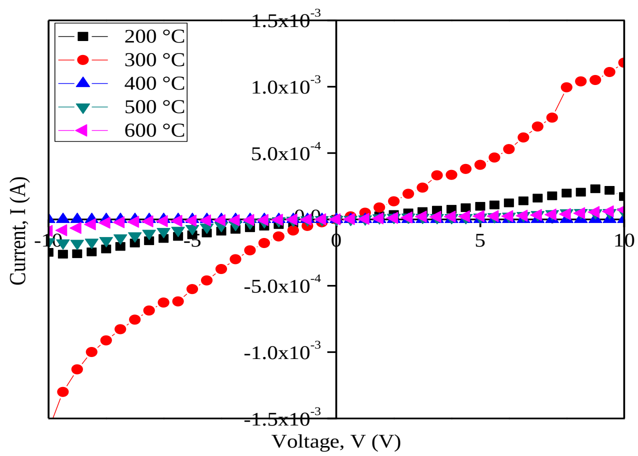


Figure 2 I-V characteristics of deposited TiO_2 thin films annealed at 200 – 600 °C for 20 min

Table 1 Resistivity and thickness of TiO_2 thin films at various annealing temperatures

Annealing Temperature (°C)	Resistivity (Ω.cm)	Thin Film Thickness (nm)
200	6.76E-03	22.428
300	2.60E-03	34.302
400	1.51E-02	54.714
500	8.41E-02	67.346
600	1.59E-01	77.212

The resistivity of thin film can be calculated using the following equation:

$$\rho = R\frac{wt}{l} \quad (1)$$

where ρ is the resistivity (Ω.cm), is the resistance (Ω), is the width of metal contact (cm) and (cm) is the length between metal contact and is the thickness (cm) of the deposited film. The calculated resistivity and thickness of TiO_2 thin films at various annealing temperatures are summarized in Table 1. Thin film annealed at 300 °C shows lower resistivity compared to other thin films and the resistivity of thin films annealed above 400 °C increases as the annealing temperature increases. From (1), the resistivity is linearly related to the thickness of deposited thin film. So, it is expected that thicker film that formed at higher annealing temperatures will result in higher resistivity. As tabulated in Table 1, thickness of TiO_2 deposited thin films increases as the annealing temperature increases. The thicker film was formed may due to the formation of denser film and also the enhanced crystal growth due to the increase in the annealing temperature.

The conductivity dependence on the annealing temperatures is plotted in Figure 3. The conductivity of deposited TiO_2 thin films is inversely proportional to the resistivity of thin films. Following equation shows the relation between conductivity (σ) and resistivity (ρ):

$$\sigma = \frac{1}{\rho} \quad (2)$$

As can be seen from the graph, the most conductive sample is annealed at a temperature of 300 °C followed with 200 °C, 400 °C, 500 °C and the least conductive is 600 °C. This result obey the equations (1) and (2) that the decrease of conductivity is due to the increase in the film thickness, which was also reported by Li-Te Yin *et.al.*, [14].

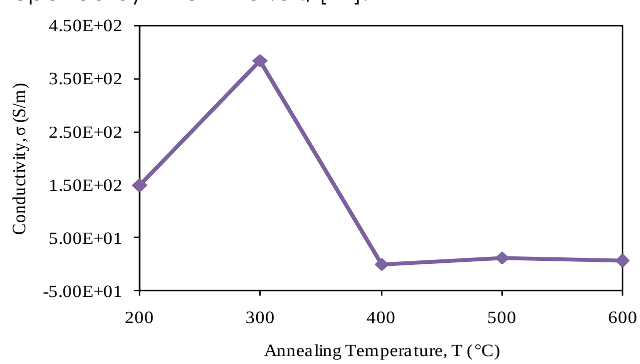


Figure 3 Conductivity of TiO_2 thin films at various annealing temperature

3.2 Surface Morphology of TiO_2 Thin Films

Figure 4 (a), (b), (c), (d), and (e) show the surface morphology images of deposited TiO_2 thin films using magnification and voltage of 50 k and 5 kV respectively. As can be seen from the images, different annealing temperature resulted in agglomerated microstructures. It shows the agglomeration of particles and a porous surface with some region not covered with TiO_2. The agglomerated particles for the sample annealed at lower temperature can be seen as larger than those annealed at a higher temperature and films formation under the agglomerated particles on the sample annealed at higher temperature can be seen clearly. Annealing at higher temperature may enhance the adhesion of the thin films to the substrate surface thus naturally produce thicker films.

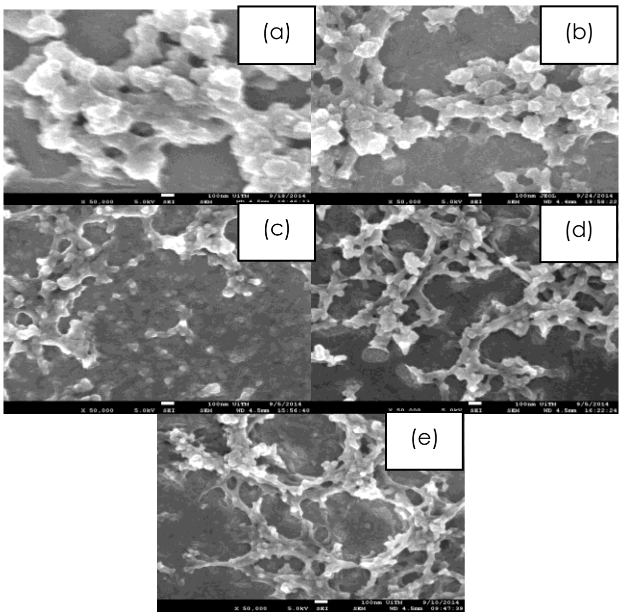


Figure 4 Surface morphology images of TiO_2 /ITO thin films annealed at (a) 200 °C (b) 300 °C (c) 400 °C (d) 500 °C and (e) 600 °C for 20 min

3.3 Crystalline Properties of TiO_2 Thin Films

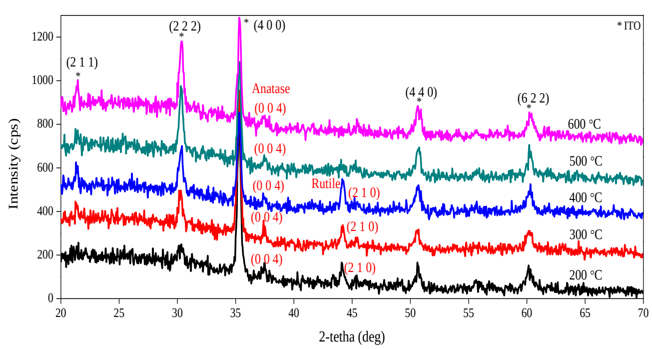


Figure 5 XRD patterns of deposited TiO_2 /ITO thin films annealed at 200 – 600 °C for 20 min

To clarify the influence of annealing temperature on the crystalline structure, an X-Ray diffraction (XRD) study was carried out. Figure 5 shows XRD patterns of TiO_2 thin films. The XRD peak of the TiO_2 films was observed at 37.5° which is identified in (0 0 4) as anatase phase. From the graph, it indicates that anatase phase appeared as early as annealing temperature at 200 °C and above. Other peaks that appeared were related to ITO substrate. The average crystallite size of the deposited TiO_2 can be estimated using the Debye-Scherrer formula as given by following equation [16-18]:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (3)$$

where D is the particle size of crystal from the measured width of their diffraction curves, k is the shape factor that usually taken as 0.9, λ is the wavelength of X-ray diffraction (Cu Ka, λ = 0.15406 nm), β is the full width of the half maximum (FWHM) of the examined peak, and θ is the diffraction angle which satisfied the Bragg's law. The crystallite sizes of anatase TiO_2 are determined from (0 0 4) peak at 2θ = 37.5 °. Based on the calculation from Eq. (3), the crystallite size of TiO_2 thin films are 23.92, 24.59, 25.69, 25.96 and 29.79 nm respectively. From the result, it is clearly that the crystallinity of thin films is improved and crystallite size of the deposited TiO_2 anatase increase as the annealing temperature increase as reported by many [18,20]. This is because, higher temperature supplies sufficient energy to the atoms to form a uniform crystal orientation [21].

3.4 EGFET Sensor Characterization

Figure 6 shows the transfer characteristics (drain current versus gate voltage, I_D-V_G) of deposited TiO_2/ITO thin film annealed at 300 °C in linear region for pH range of 4 – 12. For other annealing temperature, the transfer characteristics have similar behavior as annealed at 300 °C. It is observed that, the threshold voltage (V_{TH}) shift from left to the right with the increasing pH value is due to the decreasing of hydrogen ion concentration in pH buffer solution. The correlation between I_D and pH values can be achieved by using the basic MOSFET expression [19]. The ideal current-voltage (*I-V*) expression in linear region can be calculated by using the following equation:

$$I_{DS} = \frac{WC_{ox}\mu_n}{2L}\left[(V_{GS} - V_T)V_{DS} - \frac{V^2_{DS}}{2}\right] \quad (4)$$

where W and L is the width and length of the gate of MOSFET, C_{OX} is the gate oxide capacitance per unit area, μ_n is the carrier mobility in the channel and V_T is the threshold (turn on) voltage of MOSFET. From (4), the change of V_T depends on different pH value. The drain voltage was fixed at 500 mV and the gate voltage was varied from -2 to 3 V. The sensitivity of TiO_2/ITO thin films at various annealing temperature was calculated from the linear relation between gate voltage and the pH value as depicted in Fig. 7 where drain current (I_D) was fixed at 100 μA. Sensitivity and linearity for all deposited TiO_2/ITO thin films was listed in Table 2. It shows that thin film anneals at 300 °C exhibits the higher sensitivity and better linearity compared to others. Meanwhile, the sensitivity of TiO_2 thin film decreased to 34.21 mV/pH as annealing temperature increased at 600 °C. As reported [14], the thicker membrane reduces the pH sensitivity of the sensor. This statement was supported by our thickness of TiO_2 films as tabulated in Table 1.

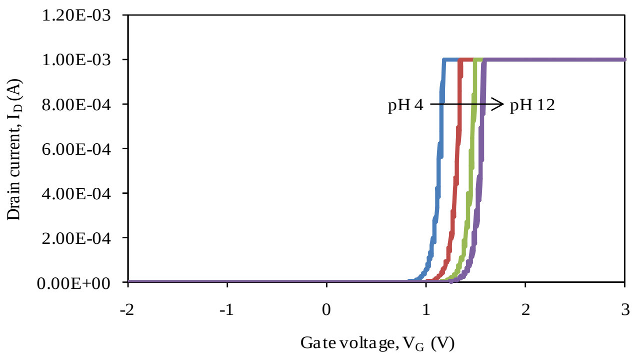


Figure 6 Transfer characteristics (I_D-V_G) curve of deposited TiO_2 thin films annealed at 300 °C in pH 4-12

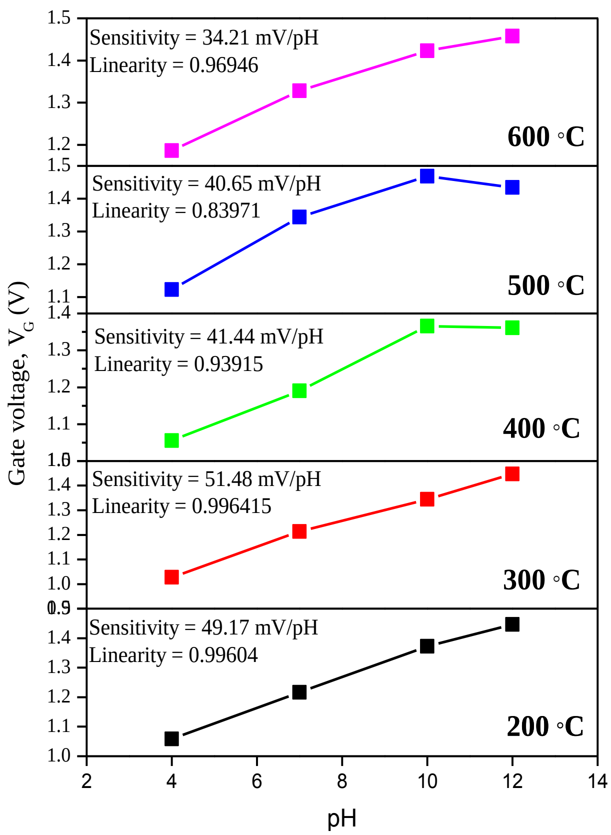


Figure 7 Sensitivity and linearity of deposited TiO_2 thin films annealed at various temperature

Table 2 Sensitivity and linearity of TiO_2 thin films at various annealing temperatures

Annealing Temperature (°C)	Sensitivity (mV/pH)	Linearity
200	49.17	0.99604
300	51.48	0.99415
400	41.44	0.93915
500	40.65	0.83971
600	34.21	0.96946

4.0 CONCLUSION

In this work, TiO_2 thin films were deposited by sol-gel spin coating technique onto the ITO substrate to be implemented as EGFET pH sensing membrane. The XRD pattern indicates that anatase phase oriented appeared as early as annealing temperature of 200 °C and above. Also, as the increasing of annealing temperature, crystallinity of thin films is improved and the average crystal size also increases due to sufficient energy to form a uniform crystal orientation. For EGFET performance, the transfer characteristic (I_D-V_G) of the deposited TiO_2/ITO thin film was obtained. A higher pH sensitivity of 51.48 mV/pH with linearity of 0.99415 was achieved for TiO_2/ITO sensing membrane annealed at 300 °C. This work also reveals the relationship between sensitivity and conductivity of thin films. The conductivity of TiO_2/ITO thin films was proportional with the sensitivity of sensing membrane.

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