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The Sensitivity Behavior of TiO_2 Thin Films-based Extended-Gate Field Effect Transistor pH Sensor

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ABSTRACT

To present highly sensitive and precise pH sensor, fabrication of metal oxide based EGFET sensor is needed. The used of TiO_2 thin films as sensing electrode for pH sensor is widely known for its best sensitive in pH measurement. The films were prepared by depositing the films onto ITO glass substrate using sol-gel spin coating method. The sensitivity and linearity of TiO_2 EGFET sensing electrode for various spin speeds (1000 to 5000 rpm) were obtained from transfer characteristic (I_{DS} -V_{REF}) and output characteristics (I_{DS} -V_{DS}) analysis. The effect of different immersion time (25, 50, and 75 s) and repeatability measurement for each sample were also investigated in this study. Among of all samples, the sensing electrode prepared at 5000 rpm spin speed with 75 s immersion time achieved the highest sensitivity of 52.20 mV/pH and good linearity of 99.64 %. Meanwhile, the sensing electrode prepared at spin speed 3000 rpm produced good repeatability and small standard deviation. The performance EGFET sensor has also been tested at different pH values (pH4, pH7, and pH10) and found TiO_2 sensing electrode showed more precise results in an alkaline (pH10).

Keywords: Extended gate field effect transistor, electrochemical sensor, pH sensor, spin coating method, titanium dioxide

1. INTRODUCTION

Recently, pH sensor gained interest by researchers to maximize its potential applications specifically in agricultural production, health monitoring, food processing, and environmental observation as well. Traditional pH sensors suffer unfit conditions in some applications due to mechanical fragility. To overcome this problem, a MOSFET-based pH sensor was developed and known as an ion sensitive field effect transistor (ISFET). The study was discovered by P. Bergveld in 1972 [1], which introduced a new solid state device for the measurement of ionic reaction in the electrochemical and biological environment. However, ISFET showed some limitations during the measurement process in dealing with temperature and light. Furthermore, it has some issues with ionic penetration as well. In 1983, Spiegel [2] proposed a simple and effective solution to overcome ISFET problems. The method of detection is known as the extended gate field effect transistor (EGFET). EGFET pH sensor provides more advantages compared to ISFET for example, good stability during measurement process in light and temperature condition, high sensitivity, low impedance and also low cost and has simple packaging too [3]–[5].

The schematic diagram of the EGFET pH sensor can be referred in Figure 1. The diagram shows cross-sectional view of FET structure and the extended connection of wire is connected to the gate of FET.

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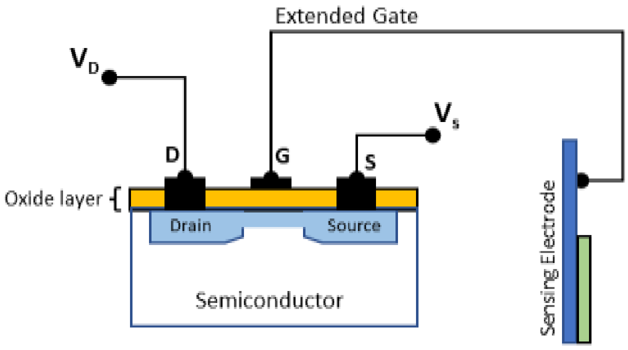


Figure 1. Illustration of EGFET schematic diagram.

Generally, every electrochemical sensor has two or three electrodes to complete the measurement connectivity. Instead of having three electrodes such as conventional electrochemical sensor, MOSFET-based sensor only requires two electrodes to create the surface potential effect between these two electrodes. Additionally, the bias voltage supplied to the reference voltage will trigger the I_{DS} value by depending on the concentration of H+ and OH- ions sensed by the sensing electrode in the solutions. Due to this evolution in pH sensors, the study created a new opportunity for the development of a sensing platform. Metal oxide is one of the sensing materials with distinctive properties on its surface that enable it to interact with hydrogen ions in liquid solutions and produce surface potential. This material is also capable of sustaining a chemical environment and has extended electrode life.

Various metal oxide has been used for instance, tantalum oxide (Ta_2O_5), titanium dioxide (TiO_2), copper oxide (CuO), zinc oxide (ZnO), and tin dioxide (SnO_2) etc [6]–[10]. Among them, TiO_2 is the most potential material that has been used in many applications. This includes memristor, dye-sensitized solar cell, photocatalysts, capacitor, gas sensor, and sensing electrode for pH detection. As a sensing electrode, TiO_2 offers good chemical stability, more sturdy and flexibility and possess high dielectric constant [11]. Numerous methods have been reported to fabricate the TiO_2 sensing electrode such as physical and chemical vapor deposition, sputtering, immersion techniques, spin coating, spray pyrolysis, electron beam deposition, and pulsed laser deposition methods. Comparing all of the techniques, the sol-gel spin coat method offers the simplest and cost-effective operation. Technically, this method delivers such a homogenous chemical reaction between the thin films and the substrate especially when dealing with high temperature[12].

The purpose is to verify the influence of spin speed variation on the sensing performance of TiO_2 films during sol-gel deposition process. It is believed that spin speed affects TiO_2 thin film thickness that can significantly contribute to the sensitivity, stability, linearity and repeatability of the pH sensor [6], [13]. Yet, none of them have reported the precision of the TiO_2 EGFET pH sensor in the acidic, neutral, or alkaline solutions. Here, we investigate the sensitivity behavior of EGFET pH sensor prepared at 1000 to 5000 rpm spin speeds.

2. MATERIAL AND METHODS

2.1 TiO_2 Sensing Electrode

The sensing electrode was prepared by cutting 2 x 2 cm^2 ITO glass into 1 x 2 cm^2 in diameter. The ITO substrates were sonicated in ethanol and deionized water for 10 minutes each. Then, the ITO substrates were dried by Argon gas. TiO_2 solution was prepared using absolute ethanol (SYSTERM, 99.8%), deionized (DI) water (Milli-Q Advantage A10), glacial acetic acid (GAA) (Friedemann Schmidt, 99.8%), Triton X-100 (R&M Chemicals, 98%), and titanium (IV) isopropoxide (TTIP) (Sigma-Aldrich, 97%). Absolute ethanol and DI water were used as solvent and TTIP was used as the precursor. Meanwhile, GAA and Triton X-100 was used as the stabilizer and surfactant respectively. First, absolute Ethanol, TTIP and GAA were mixed in a beaker. Mixture of Ethanol, deionized water and a drop of Triton X were mixed in another beaker. Both mixtures were stirred on a hot plate for 1 hour each before mixing them together. After that, the TiO_2 solution was continuously stirred for the next 1 hour and ready to be deposited on a cleaned ITO substrate using the spin coating method. Each sample was deposited at a variation of spin speed at 1000 to 5000 rpm for 60 s. After that, the samples were dried at 200°C for 10 minutes and annealed at 400 °C for 20 minutes.

2.2 Measurement Setup

The pH sensitivity measurement was performed on each prepared TiO_2 sensing electrode. Figure 2 shows the measurement setup of electrochemical EGFET pH sensor. The sensing electrode (SE) was connected to the gate of a commercialized MOSFET to form an extended gate of the MOSFET while the drain and the source of the MOSFET were connected at SMU2 and SMU3 of the semiconductor parametric device analyzer model B1500A respectively. Besides, the commercialized reference electrode (RE) was connected at SMU1 and retrieved bias voltage from the device analyzer. The purpose of RE is to complete the circuit connectivity of electrochemical pH measurement, hence create the potential effect between SE and RE. Both SE and RE were dipped in pH2 to pH12 buffer solution. Transfer I-V curve characteristic (I_{DS}-V_{REF}) and output characteristics (I_{DS}-V_{DS}) analysis was carried out according to immersion time, variation of pH buffer, and repeatability measurement as tabulated in Table 1.

Table 1 List of measurement analysis

Measurement Analysis	Variation
Immersion time	25, 50, and 75 s
pH buffer solution	pH2 to pH12
Repeatability	Set 1, Set 2

The influence of spin speed variation on the sensitivity of TiO_2 EGFET pH sensors was analyzed at 25, 50, and 75 s immersion time, represented as Reading 01, Reading 02 and Reading 03 respectively. The measurement was performed in each pH 4, pH7, and pH10 buffer solutions. The results of transfer I-V curve and output characteristic are shown for the TiO_2 EGFET pH sensor prepared at 1000 rpm as a reference in this study. The reference voltage value of transfer characteristic was extracted at 100 µA for each pH measurement. These values were plotted vs pH value in order to determine the sensitivity and linearity value of the samples which results to the sensing capability towards pH variations. For the measurement repeatability, the whole steps in SET 1 were repeated using the same sample and labeled as SET 2. The complete set of the experimental results were summarized in Table 2 and Table 3.

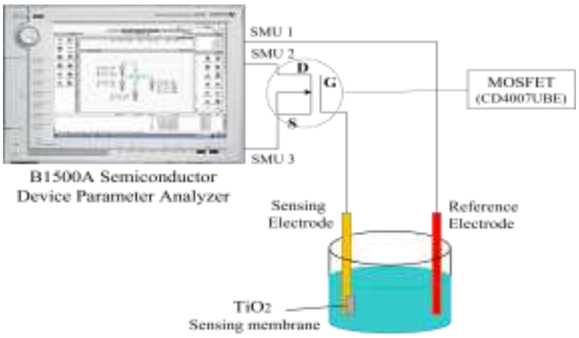
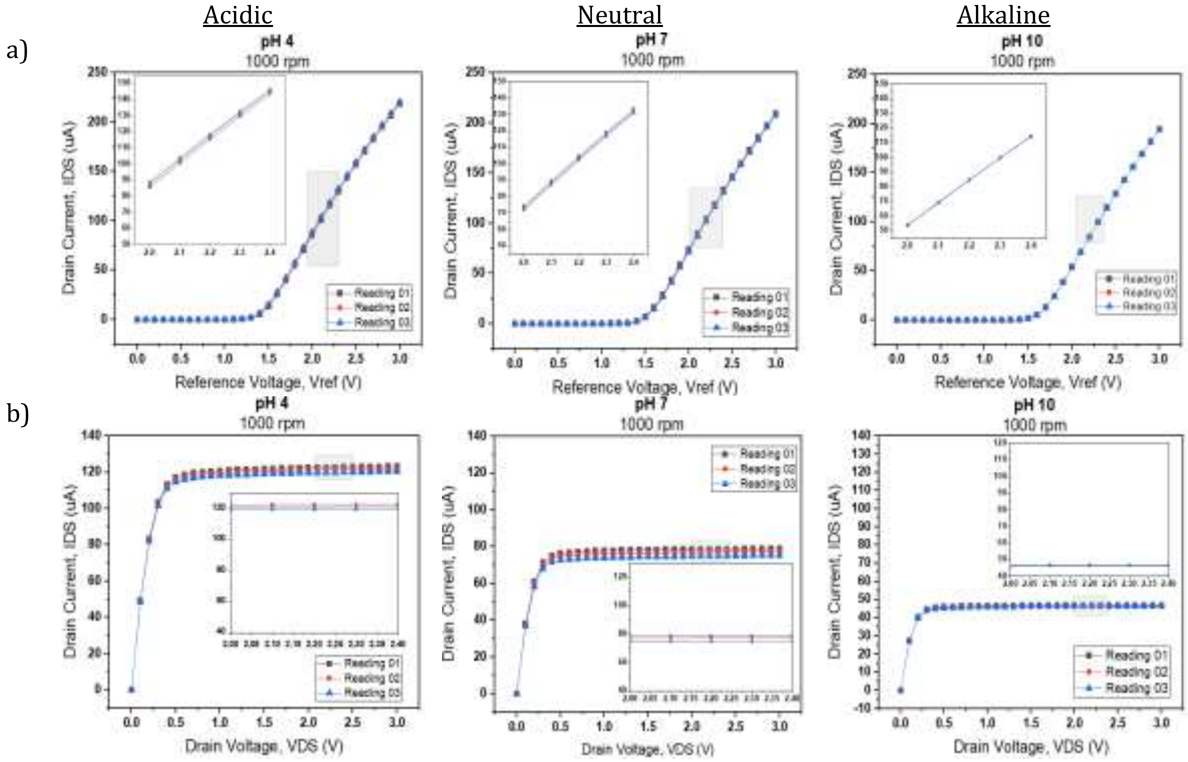


Figure 2. EGFET pH measurement setup.

3. RESULTS AND DISCUSSION

3.1 Immersion Time Dependence

Figure 3shows the transfer characteristics (I_{DS}-V_{REF}) and output characteristics (I_{DS}-V_{DS}) respectively for a sample 1000 rpm in different pH values (pH 4, 7 and 10) for 3 readings. The inset was plotted at the range of 2.0 V- 2.4 V.



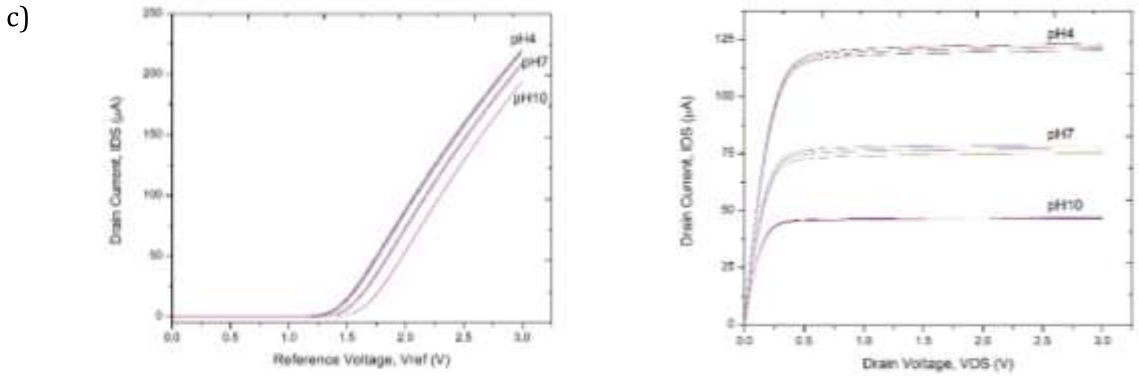


Figure 3. TiO_2 EGFET pH sensor with spin speed of 1000 rpm at different pH buffer solutions (pH4, pH7, and pH10), (a)Transfer Characteristics (I_{DS}-V_{REF}), (b) Output Characteristics (I_{DS}-V_{DS}), and (c) overlay graph at different pH value.

The enlarged views are intended to compare the curves for the three readings. The curves show a closer line to each other in alkaline solution, pH 10 compared to those of the three readings in pH 4 and pH 7. These show that the measurement readings of TiO_2 EGFET pH sensor were highly precise in alkaline solution, pH 10 followed by measurement readings of neutral solution, pH 7 and acidic solution, pH 4. The reaction between metal oxide and electrolyte during the immersion process is basically represented in Figure 4. It can be divided into three reactions according to the types of the pH buffer solution; neutral, acidic, and alkaline.

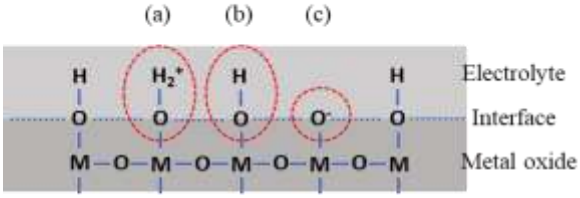


Figure 4. Basic reaction on Metal oxide surface ion's basic reaction in (a) acidic, (b) neutral and (c) alkaline conditions.

For acid, since the H^+ ion concentration in the solution is high, protonation will happen meaning that the hydroxyl (-OH) group of the metal oxide surface acquire H^+ ion and forms a positive charge surface. In alkaline solution, OH are more, thus there is more tendency for the metal oxide surface to lose the H^+ ion from the hydroxyl group which means deprotonation happens [9]. These reactions may contribute to the variation of readings seen in the results of Figure 5, in which the accuracy in the alkaline solution is higher than those in acidic. Although this phenomenon is indirectly related, the difference in the reaction process during the immersion may have some information to be discussed further.

The three reading measurements were derived from the transfer characteristic (I_{DS}-V_{REF}) curve at I_{DS} = 100 µA. The highest sensitivity, 43.80 mV/pH and linearity, 99.23%. was obtained at reading 3 as shown in Figure 5(c). On the other hand, the sensitivity and linearity of reading 1 shown in Figure 5(a) was 35.20 mV/pH and 97.22% respectively followed by the reading 2 shown in Figure 5(b) where the sensitivity was 36.30 mV/pH, and the linearity was 98.37%. This certainly showed that the change of the surface potential voltage (ψ) resided between the sensing electrode and pH buffer solutions is directly affecting the sensitivity value of the sensor. This happens due to the number of binding sites residing on the sensing electrode area, which was explained in the site binding theory in previous article [14].

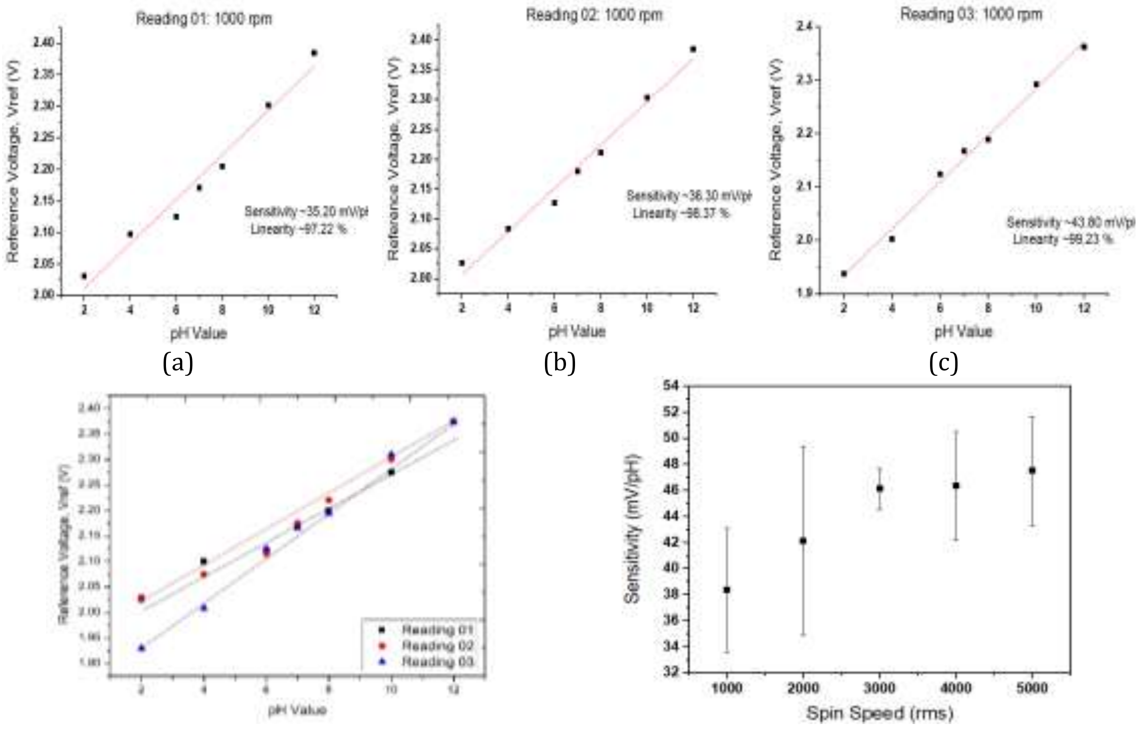
Due to the longer immersion (75 s) time, the equilibrium state at the TiO_2 surface will be affected, which may lead to the changes in electrical properties and surface potential of the sensing electrode. The changes of surface potential of TiO_2 can be described as in (1):

$$2.303(pH_{PZC} - pH) = \frac{q\psi}{kT} + \sinh^{-1}\left[\frac{q\psi}{kT}\frac{1}{\beta}\right] \tag{1}$$

where pH_{PZC} is the value of pH buffer solution at zero charge point, q is the electron charge, k is Boltzmann's constant, T is the temperature, and β is the sensitivity parameter of the gate insulators that depends on the surface density of hydroxyl groups. Based on previous study, high β was obtained when the linear response of the surface potential voltage between the sensing electrode and pH buffer solution is high [15].

Table 2 shows the pH sensing measurement results of TiO_2 EGFET pH sensor fabricated at 1000 to 5000 rpm. The measurement was performed at Reading 01, Reading 02 and Reading 03 for each sample. The pH sensitivity and linearity for each sample increases at the reading 3. In addition, the highest sensitivity of 52.20 mV/pH was obtained in this study when the sample was fabricated at 5000 rpm. The result shows the value is nearest to the ideal Nernst limit sensitivity which is 59 mV/pH [14]. The spin speed is directly affecting the thin films thickness. High spin speed causes the thickness of TiO_2 film to become thinner, which leads to low potential difference between substrate and TiO_2 thin films [15]. Thus, increasing the sensitivity of the TiO_2 sensing electrode. Meanwhile, the pH sensitivity pattern of SE can be seen in Figure 5(d), where the sensitivity of SE increases as the spin speed is increased to 5000 rpm. As for the linearity, all samples and all readings show a good linearity value approaching 1.

The standard deviation in Table 2 was determined from the sensitivity of three readings at each sample. The accuracy of pH sensitivity measurement was determined when the standard deviation was small. From Table 2, the standard deviation of sample 3000 rpm is 1.57, which is smaller than other samples. In this study, the spin coating speed effects have not significantly contributed to the readings. Large standard deviation values can be due to many factors, for example unintentional errors during experimental preparation.



(a) (b) (c)

(d) (e)

Figure 5. Sensitivity and linearity of TiO_2 EGFET pH sensor at sample 1000 rpm for different readings: (a) reading 1, (b) reading 2, (c) reading 3, (d) overlay graph of 1000 rpm sample for all readings, and (e) summary sensitivity value at spin speed dependence

Table 2 Sensitivity, linearity, and standard deviation of TiO_2 EGFET pH sensor

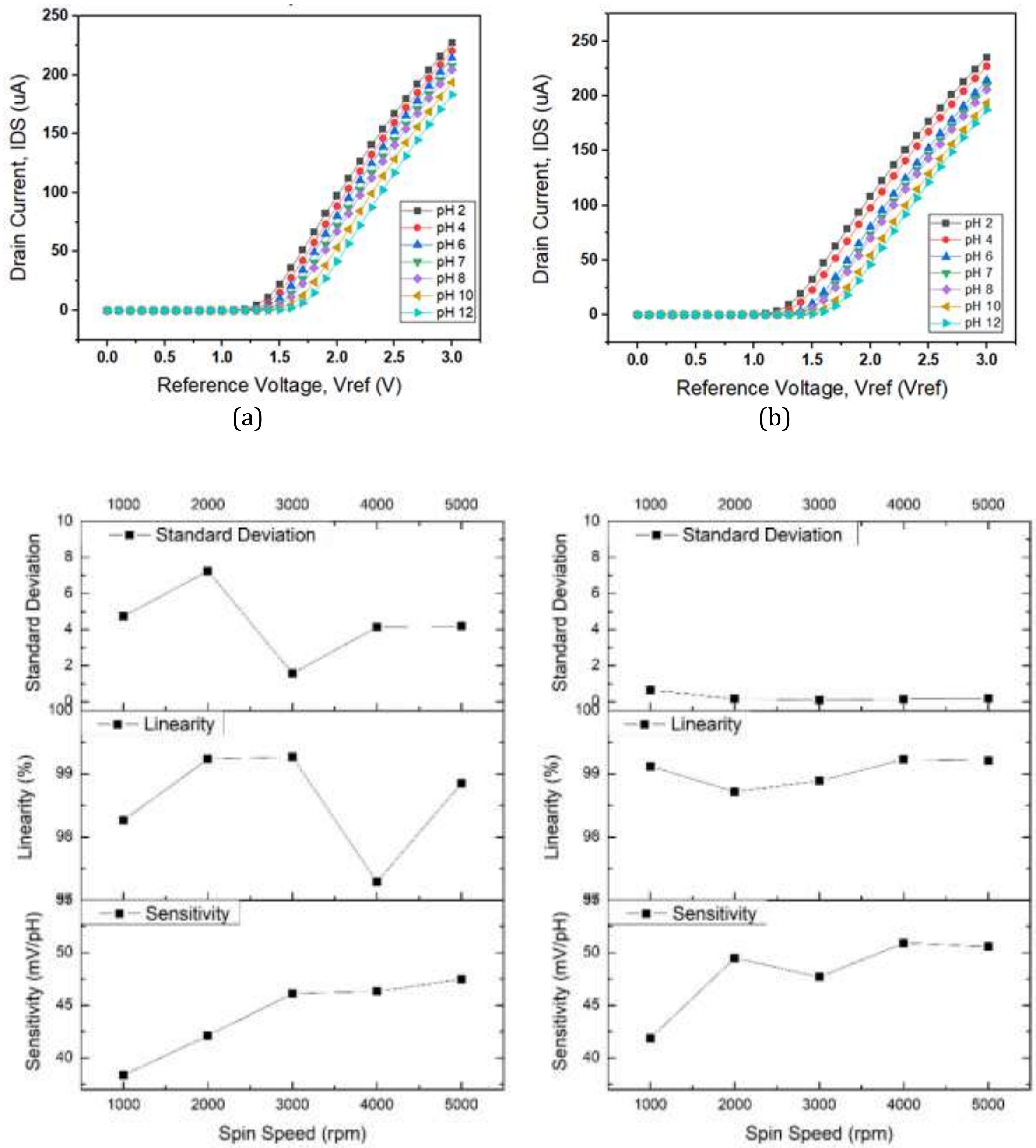
Spin Speed (rpm)	Reading	Sensitivity (mV/pH)	Linearity (%)	Standard Deviation
1000	01	35.02	97.22	4.74
	02	36.30	98.37	
	03	43.80	99.23	
2000	01	37.60	99.01	7.25
	02	38.30	99.13	
	03	50.50	99.59	
3000	01	45.60	99.27	1.57
	02	44.90	99.02	
	03	47.90	99.52	
4000	01	44.10	96.11	4.14
	02	43.80	96.04	
	03	51.11	99.71	
5000	01	46.10	98.47	3.49
	02	46.20	98.49	
	03	52.20	99.64	

3.2 Repeatability Measurement

Repeatability measurement was performed on a TiO_2 EGFET pH sensor under the same condition setup. Figure 6 shows the transfer characteristic of the TiO_2 EGFET pH sensor fabricated at 1000 rpm speed for SET 1 and SET 2. Only the results of 1000 rpm sample was represented as reference in this study. The reason is all the transfer and output characteristic graphs obtained in this study had similar trends for the rest of the sample. The compilation results of sensitivity, linearity, and standard of the TiO_2 EGFET pH sensor fabricated at 1000 to 5000 rpm speed for SET 1 and SET 2 were plotted in Figure 6 (c) and (d) respectively. Both compilation graphs were plotted with the same scale for comparison purpose. The result indicates that the standard deviation of all samples prepared at SET 2 achieved a fold lower than SET 1. The data shows that the standard deviation for sample 3000 rpm remained smallest in this study which is 1.57 and 0.10 for Set 1 and Set 2 respectively. The result proves that the TiO_2 EGFET pH sensor produced precise pH reading when the device was fabricated at 3000 rpm spin speeds. The result of all samples is summarized in Table 3.

Table 3 Compilation results of average sensitivity, average linearity, and standard deviation of TiO_2 EGFET pH sensor fabricated at 1000 rpm to 5000 rpm spin speed.

	Spin Speed	**SET 1**	**SET 2**
Average Sensitivity (mV/pH)	1000 rpm	38.37	41.90
	2000 rpm	42.13	49.50
	3000 rpm	46.13	47.70
	4000 rpm	46.34	50.93
	5000 rpm	47.50	50.60
Average Linearity (%)	1000 rpm	98.27	99.12
	2000 rpm	99.24	98.72
	3000 rpm	99.27	98.89
	4000 rpm	97.29	99.23
	5000 rpm	98.85	99.21
Standard Deviation	1000 rpm	4.74	0.66
	2000 rpm	7.25	0.17
	3000 rpm	1.57	0.10
	4000 rpm	4.14	0.15
	5000 rpm	4.18	0.20



(a) (b)

(c) (d)

Figure 6. Transfer Characteristics (I_{DS}-V_{REF}) of TiO_2 EGFET pH sensor for (a) SET 1 and (b) SET 2 of 1000 rpm sample. The compilation results for all samples, (c) SET1 and (d) SET 2).

4. CONCLUSION

In this study, TiO_2 EGFET pH sensor was fabricated using a spin coating method varied at different spin speeds. The TiO_2 sensing electrode showed more precise results in an alkaline, pH 10 solution. The TiO_2 EGFET pH sensor fabricated at 5000 rpm spin speed was observed as the optimum spin speed that resulted in high sensitivity and best linearity which were 52.20 mV/pH and 99.64% respectively. However, good repeatability performance with small deviation evidence was found at lower spin speed, which is 3000 rpm. Further analysis of the sensing behavior such as drift analysis needs to be carried out in order to support the sensor performance attained in this study.

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