STUDY EFFECTS OF THIN FILM THICKNESS ON THE BEHAVIOR OF CuS EGFET IMPLEMENTED AS pH SENSOR

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Membrane thickness is a very important parameter in controlling the sensitivity of the pH sensor and its other behaviour, such as hysteresis, repeatability, stability and reliability. Therefore, in this research work the thickness of CuS membrane was studied to find its effects on these parameters. CuS membrane was prepared from copper chloride and sodium thiosulfate dissolved in deionized water and ethanol with the ratio (7:3) then deposited on glass substrates for 60 and 150 sprays, respectively using spray pyrolysis deposition. These thin films were exposed to X-ray diffractometer and field emission scanning electron microscopy to recognize their structures and crystal shapes. Then they were used as pH sensors, so their sensitivity, hysteresis, repeatability, stability and reliability were measured. All obtained results confirmed that the membrane with low thickness (sensitivity, linearity and hysteresis 22.9 mV/pH, 93.8%, and 23.75 mV respectively) were much better than that of high thickness (sensitivity, linearity and hysteresis 7.5 mV/pH, 70.2%, and 41.37 mV respectively) as pH sensor.

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1. Introduction

pH plays important roles in many aspects, and pH sensing is very important since many fields and applications requires pH monitoring for numerous reasons. In the aspect of wound monitoring, pH act as an indicator of the state of the wound which gives information about bacterial contamination and the healing stage or for the supervision of skin grafts. Another example is in clinics, laboratories and food industries which require monitoring of pH since several chemical processes is pH dependent. Therefore, it is crucial to produce pH sensor that is fast, precise, accurate, reliable and sensitive in several applications [1].

Since Bergveld [2] employed the first field effect transistor (FET), many papers have presented how to design and develop pH sensors [3-5]. Ion-sensitive field-effect transistors (ISFETs) have been developed on the basis of metal oxide semiconductor field effect transistor (MOSFET) to measure pH and a variety of other ions. The difference between ISFET and MOSFET is that there is no metal gate electrode, given the gate is directly exposed to the buffer solutions [6]. The development of ISFET has been going on over than 35 years, and the first sensitive membrane to be used was silicon dioxide (SiO_2), which showed an unstable sensitivity and large drift. Several dielectric membranes, including Si_3N_4, Al_2O_3, SnO_2 and Ta_2O_5 [2], have been used as pH-sensitive membranes because of their higher pH response as ISFET-pH sensor. Some problems of the ISFET configuration can be overcome by using the structure of the extended gate field effect transistor (EGFET) [6]. This structure has a lot of advantages, such as light sensitivity, simple to passivate and package [7], the flexible shape of the

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extended gate structure is another advantage of the EGFET. The EGFET has better long-term stability because ions from the chemical environment are excluded from any region close to the FET gate insulator. The sensitive layered structure of the EGFET is fabricated on the end of the signal line extended from the FET gate electrode [6].

Muhammad AlHadi Zulkefle, etc. [1], Pin-Chuan Yao, etc. [8], studied the effects of increasing sensing membrane thickness on the decreasing membrane sensitivity because the increase in thickness will affect the interface between substrate and the sensing membrane where it would cause potential difference on that area, resulting in decrease of I_{ds} which will then decrease the sensitivity of the sensor.

In the past few decades, there has been an increasing investigation in semiconducting chalcogenide thin films, which have been due to their wide applications in various fields of science and technology [9]. Among them, copper sulfide is the most commonly used material. The copper sulfide thin film attracts the attention of many researchers mostly due its semiconducting properties. Also, the constituent elements of this material (Cu and S) are non-toxic and abundant in nature [10].

Thickness effects of CuS membrane sensing on the sensitivity and other pH sensor parameters were investigated in this research work, as to the best knowledge of the authors this work is the first for CuS membrane sensing. Deionized water with ethanol in the ratio (7:3) was used as the solvent for this membrane sensing preparation.

2. Methodology

2.1 Thin film preparation

Copper sulphide was prepared using two precursors ($CuCl_2$ and $Na_2S_2O_3$) as sources of Cu^{2+} and S^{2-}, respectively. These precursors were dissolved with (deionized water:ethanol) with the ratio of (7:3), and then 0.4 M concentration of both $CuCl_2$ and $Na_2S_2O_3$ were mixed to construct CuS, which was deposited on glass substrate using spray pyrolysis deposition. Deposition temperature was 200 °C and the distance between the airbrush nozzle, and the substrate was 30 cm. Starting deposition with 10 sprays (1 sec on/1 sec off) then turn off the nozzle for 1 min to keep the temperature stable then repeat this cycle for 6 times to obtain low thickness thin film. While repeating, it 15 times led to constructing high thickness thin film. Both structural and morphological properties were studied for these thin films, and then they were ready to implement as pH sensors and applied to them all the pH measurements.

2.2 Characterization techniques

PANalytical using X-ray diffractometer (XRD) equipped with CuKα source (λ=0.15418 nm) was used to check the phase purity and crystal structure. NOVA NANOSEM 450 field emission scanning electron microscopy (FESEM) was used to obtain morphological observations. And finally for sensing measurements; Keithley, Semiconductor Characterization System (2400-SCS) was used to measure pH sensitivity, hysteresis, repeatability, stability and reliability.

2.3 pH sensing system setup

pH measurements include measuring the sensitivity, hysteresis, repeatability, stability and reliability. For sensitivity, repeatability, stability and reliability measurements, the system shown in Figure (1-a) was used while for hysteresis measurement, the system shown in Figure (1-b) was used.

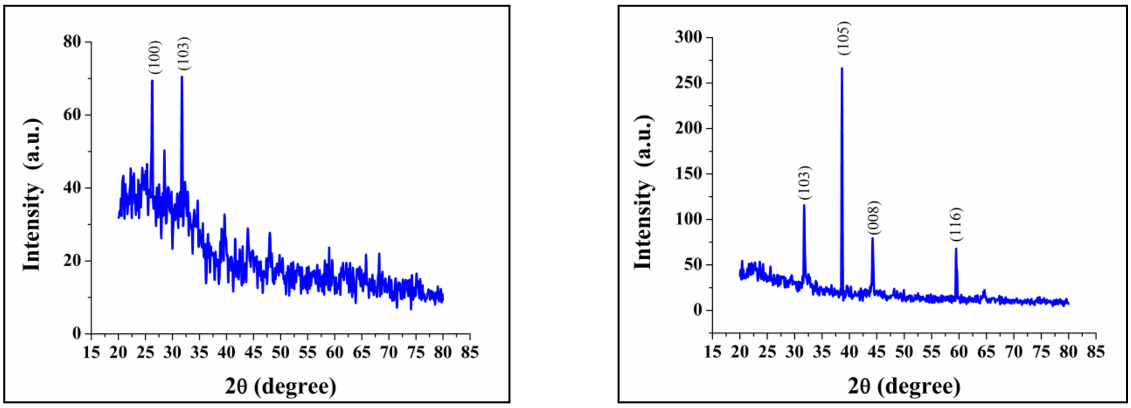
a) *b)*

Fig. 1. pH sensor setup for (a) (I-V) measurement (b) (V-T) measurement.

3. Results and Discussion

3.1 Structural Analysis

As can be seen from Figure 2, the low thickness membrane had more reflection peak intensity and better crystalline than that of high thickness membrane. Even the shared reflection (103), had a peak intensity of approximately 70 for high thickness while it been close to 125 for low thickness. The crystalline size for these membranes was calculated using Scherrer equation; the averaged crystalline size was found to 11.56 nm and 28.28 nm for high and low thickness membranes, respectively. The XRD images for both membranes showed that they constructed of pure CuS covellite phase with hexagonal crystal.

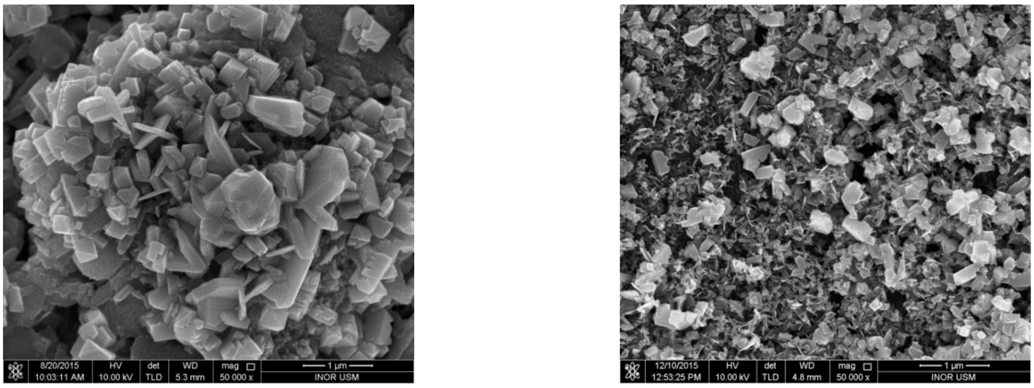


(a) (b)

Fig. 2. XRD images of CuS thin film with (a) high thickness (b) low thickness

3.2 Topography Characteristics

As can be seen from Fig. 3, the crystallinity structure of the two membranes was the same with the difference in the size of particles. It was very clear that the square-like shaped grains with nanoplates appeared for high thickness membrane was greater than that of the low thickness membrane. Because increasing the thickness results in agglomeration of CuS which caused increasing in thin film surface roughness, this would be responsible for the increasing of the particles.

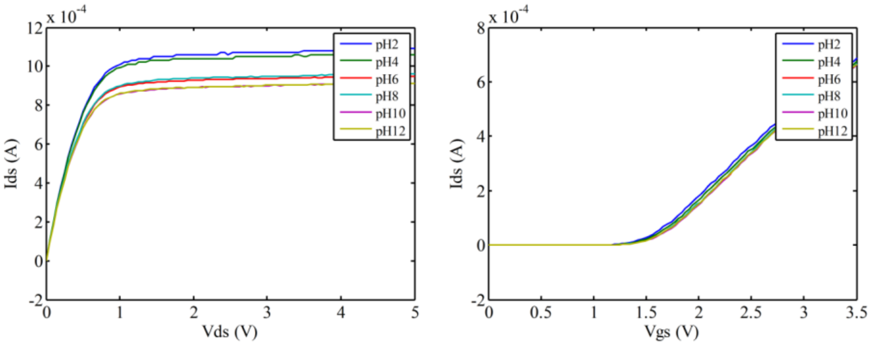


(a) (b)

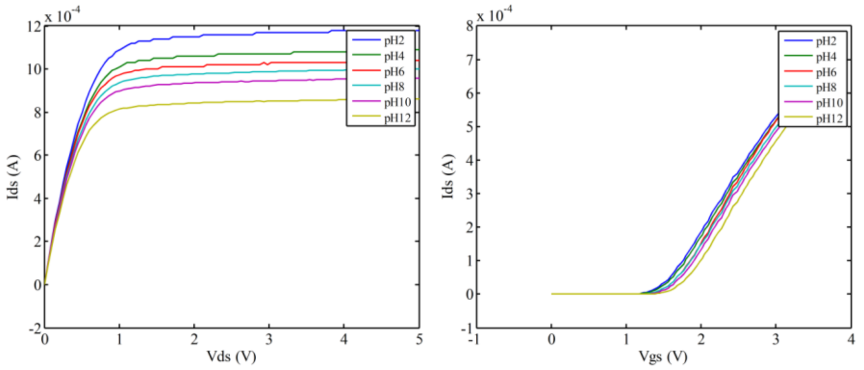
Fig. 3. FESEM images of CuS thin film with (a) high thickness (b) low thickness

3.3 pH Sensitivity and Linearity

Using setup shown in Fig. (1-a) with gate-source voltage (V_{gs}) of 3 V for saturation regime and drain-source voltage (V_{ds}) of 0.3 V for linear regime, many curves were plotted for both regimes using buffer solutions from pH2 to pH12 step 2. These curves were illustrated in Figure 4 for both membranes as (I_{ds}-V_{ds}) curve for saturation regime and (I_{ds}-V_{gs}) curve for linear regime. As can be seen, from these curves, the drain-source current (I_{ds}) also dropped threshold voltage (V_{th}) deceased due to increased membrane thickness [1,8].



(a)



(b)

Fig. 4. Output characteristics of CuS EGFET pH sensor with (a) high thickness (b) low thickness

These curves were translated to other curves shown in Figure 5 to calculate the sensitivity and the linearity for CuS membranes, the result was as follows; sensitivity and linearity for high thickness membrane were 18.8 µA/pH, 85.5% and 7.5 mV/pH, 70.2% of saturation and linear regimes, respectively. And sensitivity and linearity were 28.9 µA/pH, 96.8% and 22.9 mV/pH, 93.8% of saturation and linear regimes, respectively for low thickness membrane. These results confirmed that the increasing in membrane thickness caused decreasing sensitivity.

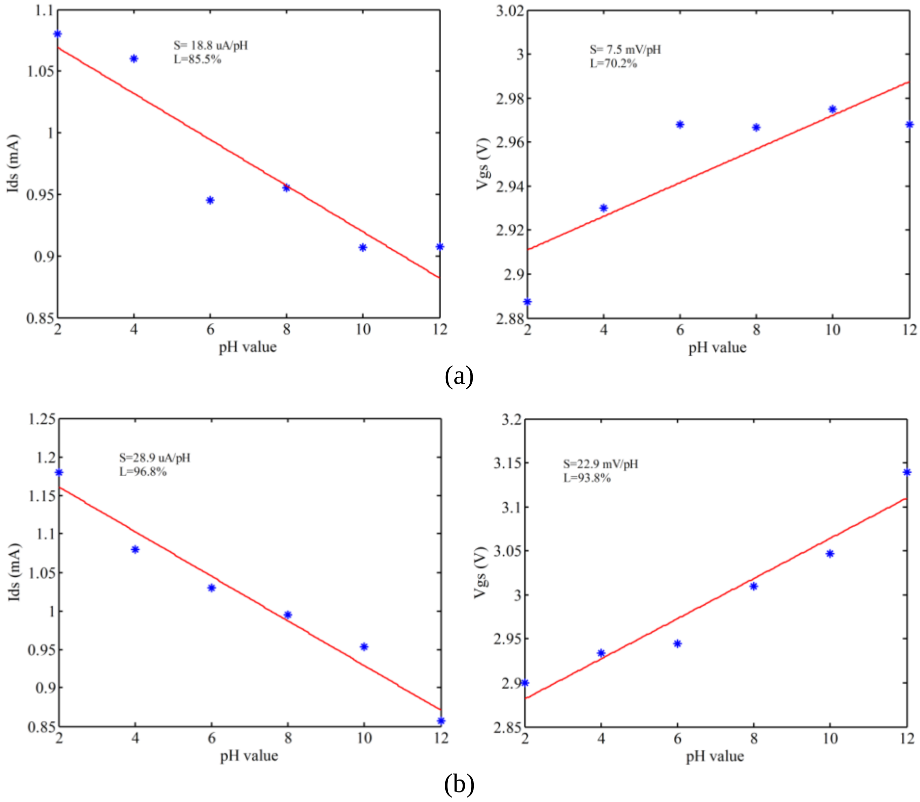


Fig. 5. Sensitivity of CuS EGFET pH sensor with (a) high thickness (b) low thickness

3.4 Hysteresis

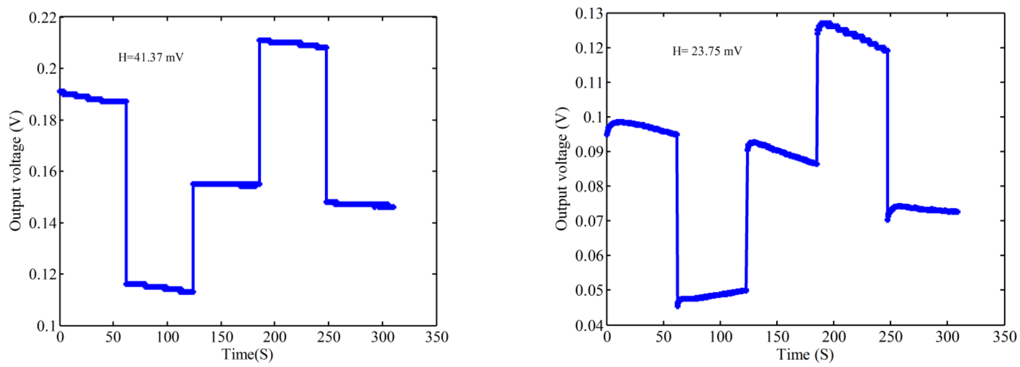
Hysteresis is known to be related to chemical interaction between ions in an electrolyte and slow reacting surface-sites underneath the membrane surface and the surface defects of the membrane [11]. The semiconductors have a significant density of structural defects between the conduction band and valence band, presenting the pinning of Fermi level when contacting a liquid electrolyte solution. Therefore, the structural defects play a role as similar as a junction of semiconductor metal [12].

The change of the pH buffer solution will proportionally affect the interface potential of the solution and EGFET sensing membrane. The output signal can be expressed as [12]

$$V_{OUT} = V_{IN}^{+} - V_{IN}^{-} = V_{REF} - V_{SENSING-FILM} \quad (1)$$

Where V_{IN}^{+} and V_{IN}^{-} are the two input terminal voltages of the Keithley. V_{REF} and $V_{SENSING\text{-}FILM}$, are the voltages of reference electrode and the sensing membrane.

The result obtained from Figure 6 which was performed using system shown in Figure (1-b) confirmed that the high thickness membrane had a lot of defects which affect its hysteresis to be 41.37 mV, while for low thickness membrane it was fewer defects so the hysteresis was 23.75 mV which seems acceptable compared to Jung-Lung Chiang etc. [13], hysteresis for amorphous tungsten oxide was 26 mV.

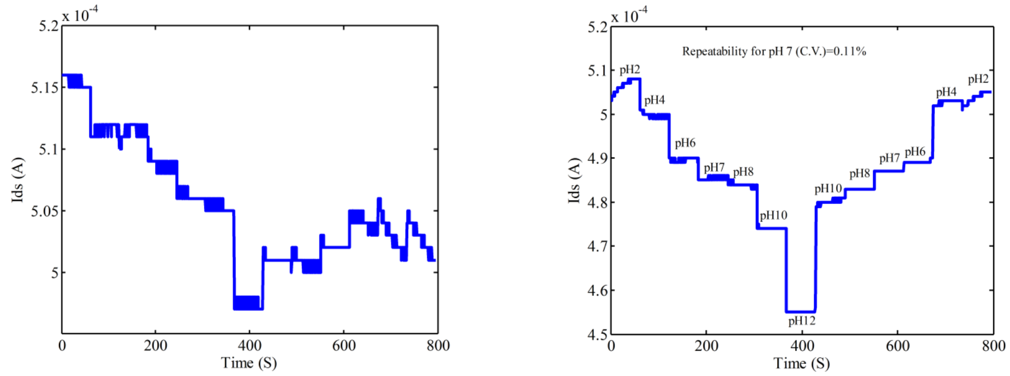


(a) (b)

Fig. 6. Hysteresis of CuS EGFET pH sensor with (a) high thickness (b) low thickness

3.5 Repeatability

The repeatability parameter important for the sensing membrane to find its validity to perform as pH sensor. The repeatability results shown in Figure 7 illustrate that the high thickness membrane had not good repeatability, in the opposite of low thickness membrane with its repeatability 0.11% as Coefficient Variation (C.V.) for pH7. So this would be another parameter confirmed that low thickness membrane preferred rather than high thickness membrane as pH sensor.

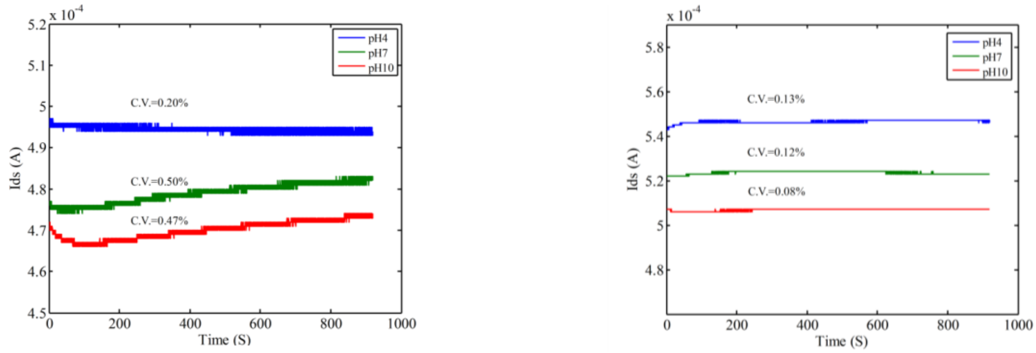


(a) (b)

Fig. 7. Repeatability of CuS EGFET pH sensor with (a) high thickness (b) low thickness

3.6 Stability and reliability

The last parameter in this research work to confirm priority of low thickness membrane was stability and reliability. As shown in Figure 8, the stability and reliability for low thickness membrane was much better than that of high thickness membrane. The stability and reliability were calculated from the curves illustrated in Figure 8 as the Coefficient Variation (C.V.). The results were 0.20%, 0.50% and 0.47% for pH4, pH7 and pH10, respectively, for high thickness membrane, while the results for low thickness membrane were 0.13%, 0.12% and 0.08% for pH4, pH7 and pH10, respectively.



(a) (b)

Fig. (8) Stability and reliability of CuS EGFET pH sensor with (a) high thickness (b) low thickness

4. Conclusion

CuS thin films were deposited using spray pyrolysis deposition using (deionized water: ethanol) with the ration of (7:3) as a solvent for the precursors. Two thin films were deposited on a glass substrate with different thickness, the first one with 150 sprays and the second with 60 sprays. After exposing these membranes to XRD and FSESM to study their characteristics, they were exposed to pH sensor measurements to find which one can be performed as pH sensor. Sensitivity (28.9 µA/pH and 22.9 mV/pH), hysteresis (23.75 mV), repeatability (0.11%), stability and reliability (0.13%, 0.12% and 0.08% for pH4, pH7 and pH10, respectively) ensured that low thickness membrane was much better than high thickness membrane and can be performed as a pH sensor. The membrane thickness affects its sensitivity since the charge of the bulk material will influence the surface charge and cause less sensitivity.

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