

Short Communication

Effect of Light on the Sensitivity of CuS Thin Film EGFET Implemented as pH Sensor

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The lightness and darkness affect the sensitivity of thin films considered as extended-gate field-effect transistor (EGFET) for pH sensor, for this reason the research work was investigated to study these effects for CuS thin film. CuS thin film prepared by copper chloride and sodium thiosulfate using deionized water as a solvent, deposited on a glass substrate by spray pyrolysis deposition. The structural properties were studied through X-ray diffractometer, and the morphological properties were studied through field emission scanning electron microscopy. Then this thin film was used as an extended gate of the field effect transistor to be implemented as pH sensor. The sensitivity was measured for this extended gate under two conditions; dark and light source. The results showed the highest sensitivity (23 mV/pH) and less hysteresis (2.6 mV) and drift (13.1, 73.5 and 85.8 for pH4, pH7 and pH10, respectively) of the sensor in dark. While under high-intensity white light the sensitivity was (19 mV/pH) and the hysteresis had the value (5.2 mV) and drift values were (21.7, 155.8 and 90.4 for pH4, pH7 and pH10, respectively). This confirmed that the extended gate of the field effect transistor is sensitive to light, and the light decreased the pH sensitivity.

Keywords: CuS thin film; EGFET; light; sensitivity; pH sensor.

1. INTRODUCTION

Metal oxide semiconductor field effect transistor (MOSFET) has been used to improve the ion sensitive field-effect transistors (ISFETs). Field-effect transistor (FET) was first employed in neurophysiological measurements by Bergveld in 1970, and then ISFETs was developed to be a new

type of chemical-sensing electrode. Several studies and research works have been published to explain the behaviour of such chemical-sensing electronic device [1].

The slow response which refers to the ion exchange of the Ta₂O₅ gate ISFET was first investigated after illumination by Voorthuyzen and Bergveld [2]. Their study focused on relaxing long-term output in the ISFET after the light switch on and off. They concluded that the polarization or charge injection processes were the cause of slow response of the ISFET after illumination. Subsequently, Tarantov et. al. [3] made many experiments like those of Voorthuyzen and Bergveld. They concluded that the positive charge generated in the insulator which responsible for a threshold voltage variation is the cause of current long-term relaxation in the Ta₂O₅ gate ISFET after light switch on and off [4]. Liao et. al. [4] studied the optical characteristics of the ISFET in different light conditions. They presented the results of affecting ISFET structure by light; they used Al as a light shield for a membrane and showed an effective decrease in the light sensitivity.

The open gate structure of ISFET makes its elements easily affected by potential effect. Due to separate structure EGFET framework, the light cannot directly irritate the channel, so only surface potential of sensitive membrane will be influenced by light [5].

In order to isolate FET from exposing to chemical environments and not to be affected or interacted with such environments, EGFET which refers to the membrane gate deposited on the line extended from the FET, is used to isolate it from those environments. This structure must be light insensitivity, flexible in use and can be constructed and packaged in simple way, etc., such advantages must be considered when nominate any membrane to be EGFET [6].

Noh, et. al. [7], investigated the light effect of ISFET of Si₃N₄ pH sensor. They concluded that the sensor behaviour (sensitivity, hysteresis and drift) in dark shows the best performance because it avoids the influence of light.

Many reports on ISFET devise structure exposed to light source have been published during few last years. Those studies and research works proved that the light effects are impediment on the behaviour of the EGFET sensors. PN junction of the source and drain in the structure is one of the factors of these effects. Theoretically, electrons in the substrate when exposed to light energy will absorb, excite and jump from their level, hence creating electron-holes pairs. These free electrons and holes will move across the depletion region by the voltage drop, this movement will generate the photocurrent. Due to the open gate configuration of ISFET, the threshold voltage will be affected by the intensity and spectral distribution of light; this will influence the sensor performance [7].

Chen, et. al [8], studied the overall characteristics of five structure EGFETs. These characteristics include sensitivity, linearity, hysteresis, drift rate, temperature effects, optical influences and sensitive area of these sensitive structures when exposing to chemical solutions (buffer solutions with different pH values).

In this research work, CuS thin film was selected to be an EGFET for pH sensor. And when applied two conditions of measuring; in the dark and under light source, the obtained results illustrate the differences in sensitivity and which measurement condition was better for the membrane. According to the best knowledge of the authors, this research work is novel and this measuring is the first for this membrane.

2. METHODOLOGY

2.1. Thin film preparation

CuS thin film can be prepared easily by spray pyrolysis deposition (SPD) because the precursor materials (CuCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$) are cheap and available in nature; also, SPD is a very simple method for deposition and not need many devices or expensive instruments, and it supplies good homogenous film. The spray system consists of compressor, timer, valve, heater, nozzle, thermal delay and fume hood. In this research, 0.4 M concentration of both CuCl_2 and $\text{Na}_2\text{S}_2\text{O}_3$ were mixed using deionized water and then deposited on the glass substrate, the deposition temperature was 200 °C, the distance between the nozzle and the substrate was 30 cm. Structural and morphological characteristics were examined for as-deposit thin film, and then it was ready for pH sensitivity measurements.

2.2. Characterization techniques

PANalytical using X-ray diffractometer (XRD) equipped with $\text{CuK}\alpha$ source ($\lambda=0.15418$ 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. Finally, for sensing measurements; Keithley, Semiconductor Characterization System (2400-SCS) was used to measure pH sensitivity.

2.3. pH sensing system setup

The system used to measure pH sensitivity was illustrated in Figure 1; it consists of two Keithley devices, PC, reference electrode, MOSFET, sensitive membrane, cavity, and buffer solutions.

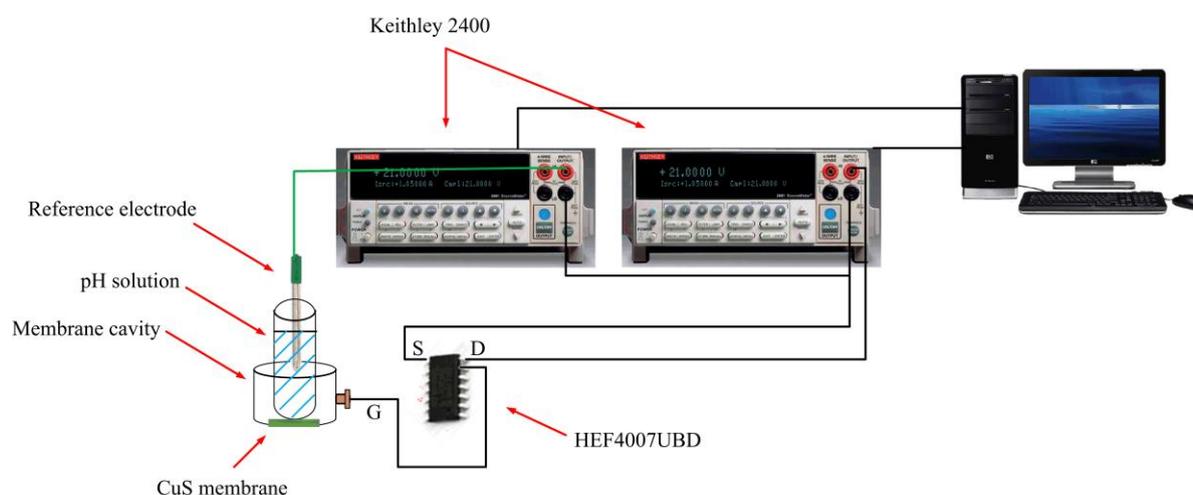


Figure 1. pH sensitivity setup

The system shown in Figure 2 was used to measure the hysteresis and drift characteristics of the sensitive membrane.

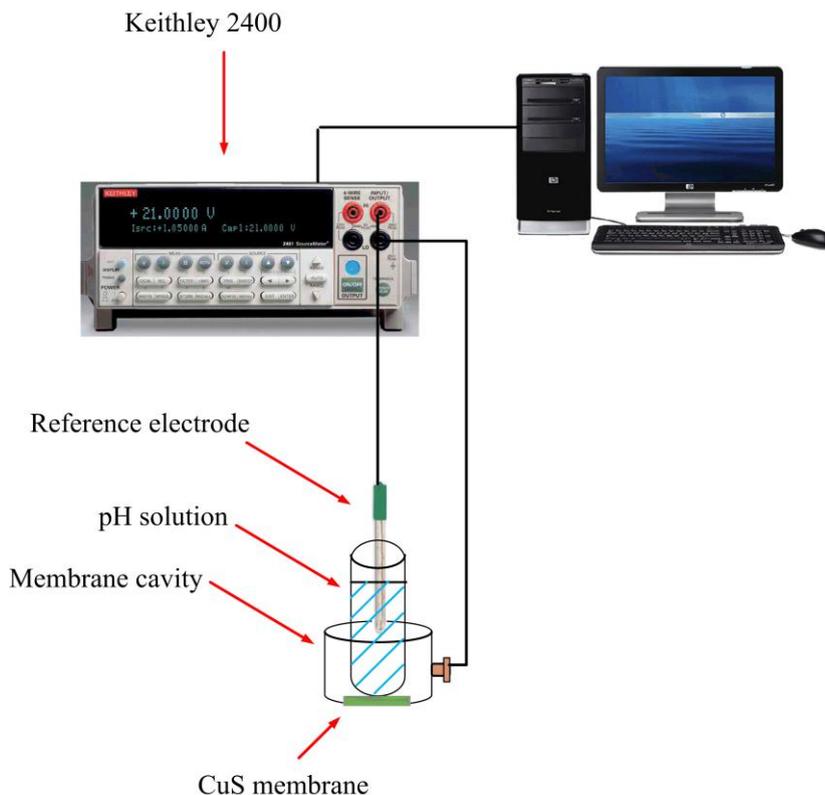


Figure 2. Hysteresis and drift measurement setup.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis

The structural properties for CuS thin film as examined by XRD showed that this film constructs of pure CuS covellite phase with diffractions (103) and (206) with a hexagonal crystal structure. But as can be seen from Figure 3; the diffraction (103) was very strong compared to (206), so this film can be considered as a single crystal thin film.

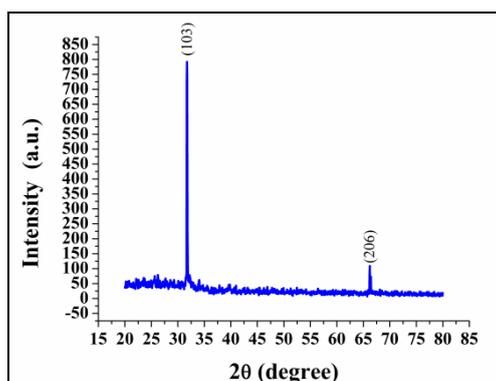


Figure 3. XRD image of CuS thin film

3.2. Topography Characteristics

FESEM image illustrated in Figure 4 showed a homogeneous deposition and well-shaped crystals, with few agglomerations. The availability of such agglomerations can be achieved as a result of the heater used through the deposition and thermal distribution for the substrate during deposition.

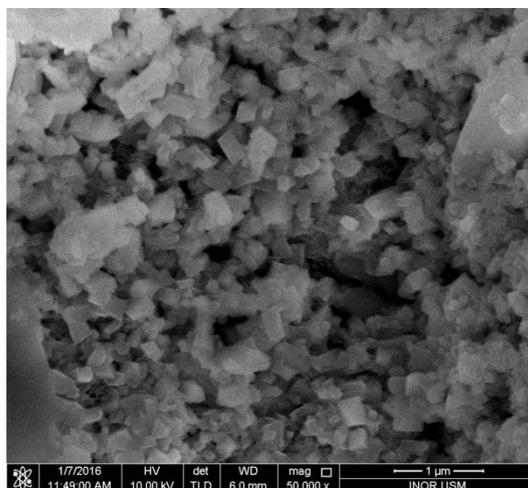
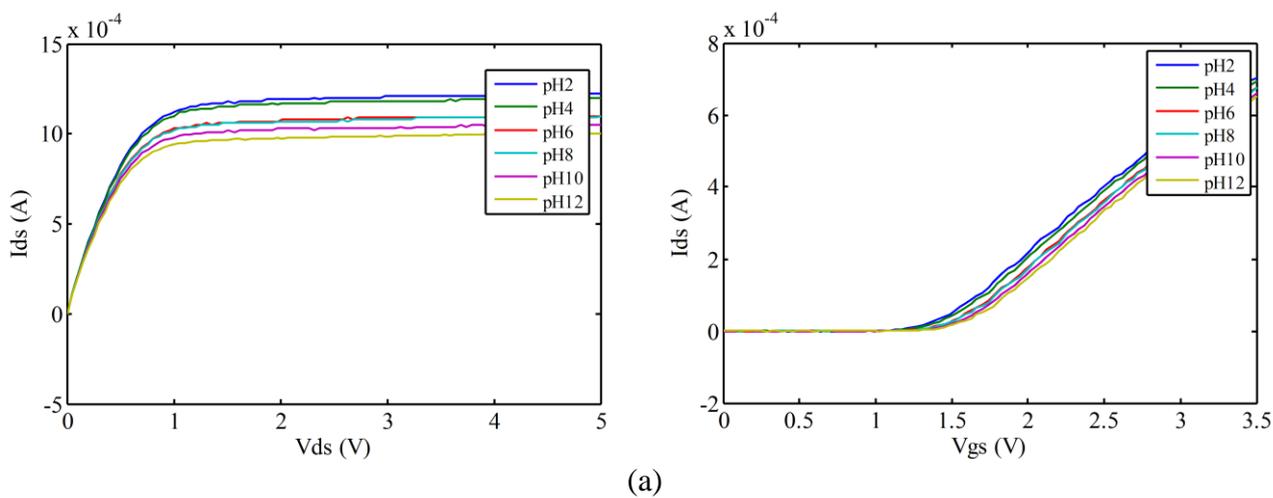
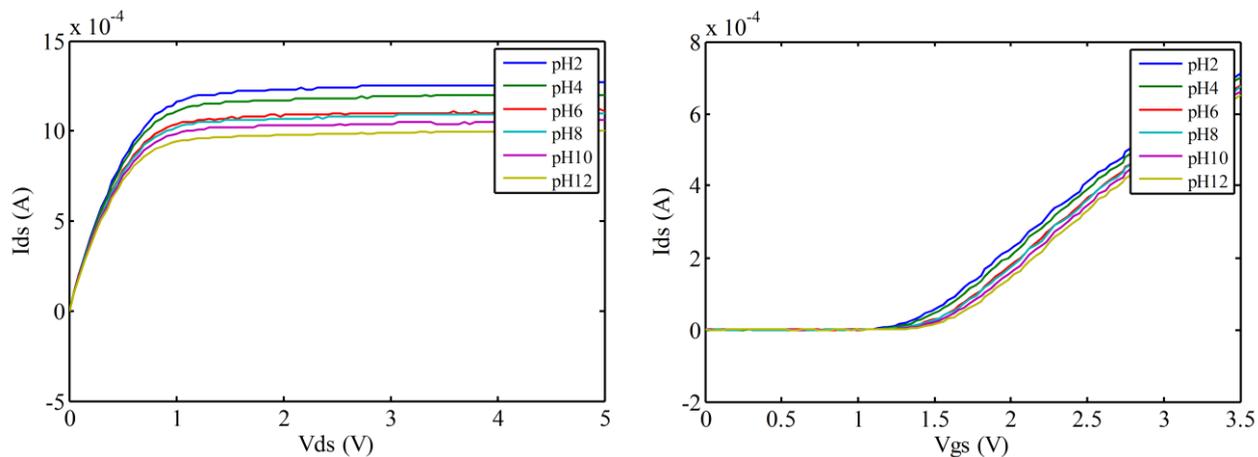


Figure 4. FESEM image of CuS thin film

3.3. pH Sensitivity and Linearity

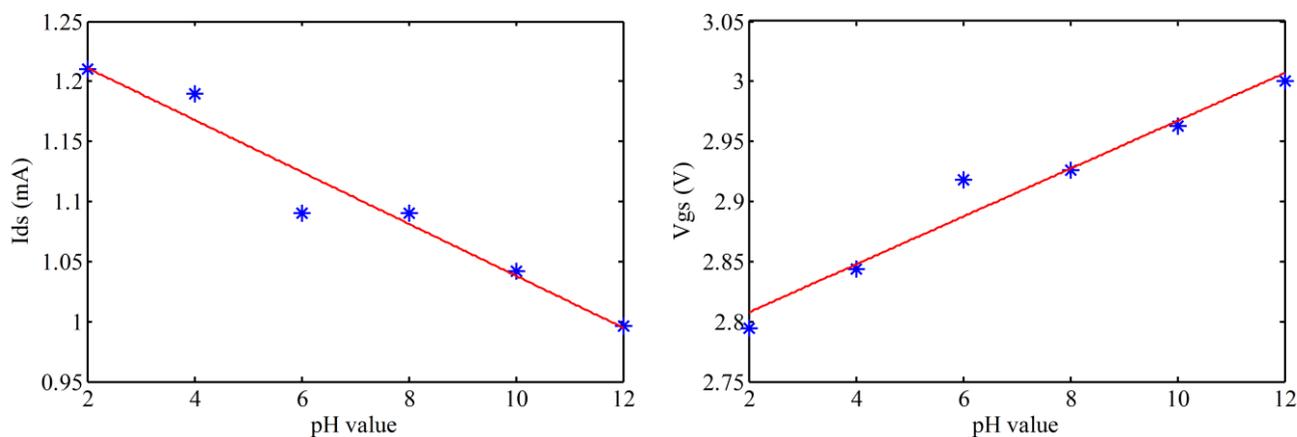
The system shown in Figure 1 was used to measure the (I_{ds} - V_{ds}) & (I_{ds} - V_{gs}) curves for saturation and linear regime, respectively; where I_{ds} , V_{ds} and V_{gs} are the drain-to-source current, drain-to-source voltage and gate-to-source voltage, respectively. Two measurement conditions were applied; in the dark and under the light source as shown in Figure 5. For the saturation regime; V_{gs} was constant at 3 V, and for linear regime; V_{ds} was constant at 0.3 V using a set of buffer solutions pH (2-12) step 2.



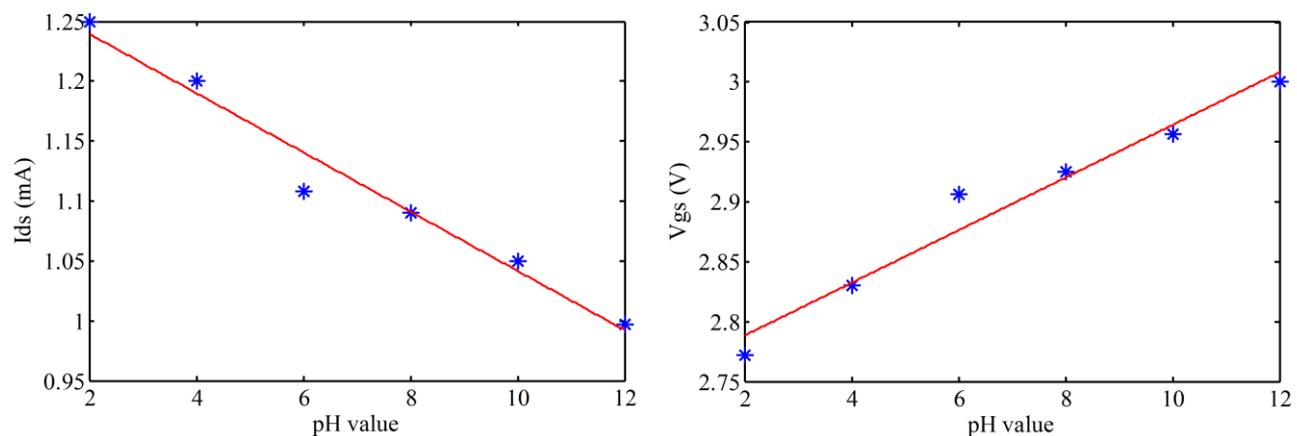


(b)

Figure 5. (I_{ds} - V_{ds}) & (I_{ds} - V_{gs}) curves of saturation and linear regime, respectively in (a) light source (b) dark



(a)



(b)

Figure 6. Sensitivity and linearity for saturation and linear regime, respectively in (a) light source (b) dark

Then from (I-V) curves shown in Figure 5, the sensitivity and linearity were calculated for saturation and linear regime, respectively. The membrane under light source showed the sensitivity of 20 μ A/pH and 19 mV/pH with the linearity 94.9% and 95.9%, respectively. While in the dark, the

sensitivity 25 $\mu\text{A}/\text{pH}$ and 23 mV/pH and the linearity 96.9% and 96.5%, respectively, as shown Figure 6. As can be seen, from these results the best sensitivity for the membrane was in dark, while it's affected when exposed to light with high intensity because the light generates hole-electron pair, when the electron exposed to light it gains and absorbs excessive energy that make it move from its level and leaving a hole. This will affect the threshold voltage of the membrane [7], which emphasizes that; the membrane should be insensitive to light to get best pH sensitivity.

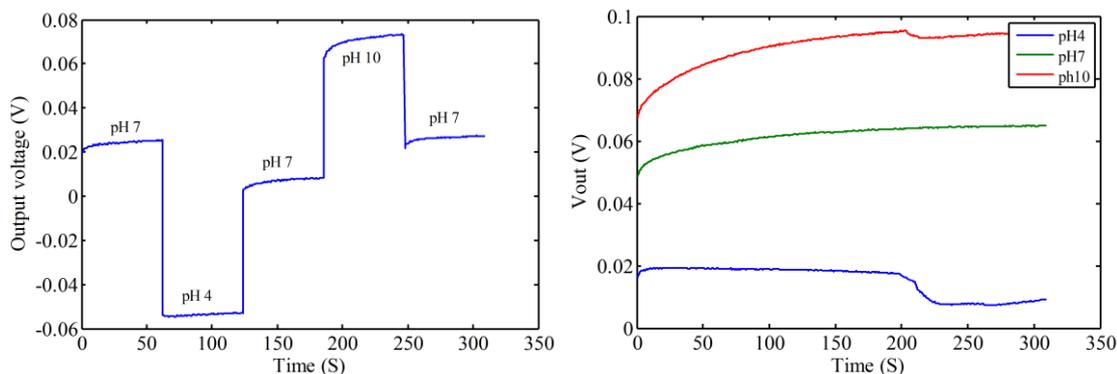
3.4. Hysteresis and Drift

Hysteresis refers to the chemical interaction between the ions of the underneath the membrane surface and the defects of the surface and the ions in the electrolyte, which is considered as the delay of pH sensor. Ion exchange will happen when the membrane immersed in the buffer solution; this process can be expressed as the interaction between the $[\text{H}^+]$ ions of the solution and the metal ions available in the surface of the membrane. The output voltage depends on this interaction, and on the charge that generates between the membrane gate and the reference electrode; the difference between the membrane gate and the reference electrode named hysteresis.

Hysteresis was measured for this membrane in the two conditions; under light source to be 5.2 mV and in dark to be 2.66 mV. Figure 7 showed hysteresis performance in pH loop (7-4-7-10-7) in 5 minutes. The hysteresis in dark has the minimum value which matched with Noh, et. al. [7].

Drift behaviour under light source and in dark was measured in this research work at different buffer solutions (pH4, pH7 and pH10) in 5 minutes. This behaviour characterizes the durability of the sensor, and it could be attributed to the $[\text{H}^+]$ ions adsorption.

Figure 7 (right side) showed the drift rate of the CuS membrane under light source and in dark; which were found to be 21.7 $\mu\text{V}/\text{s}$ (pH4), 155.8 $\mu\text{V}/\text{s}$ (pH7) and 90.4 $\mu\text{V}/\text{s}$ (pH10) under light source and 13.11 $\mu\text{V}/\text{s}$ (pH4), 73.5 $\mu\text{V}/\text{s}$ (pH7), 85.8 $\mu\text{V}/\text{s}$ (pH10) in dark. The drift rate results confirmed that the performance of CuS sensitive membrane in dark is better than that under light source. N. Noh, et. al. [7], measured the drift in dark to avoid the sensor being influenced by light, and it obtained small values of drift which is the best performance of the sensor. The pH characteristics of CuS sensor were illustrated in Table 1 and compared with other sensors. Si_3N_4 sensor presented best performance and behaviour of the sensitive membrane in dark, because it avoids the light influences on the structure of the EGFET, which confirms the results obtained in this research work.



(a)

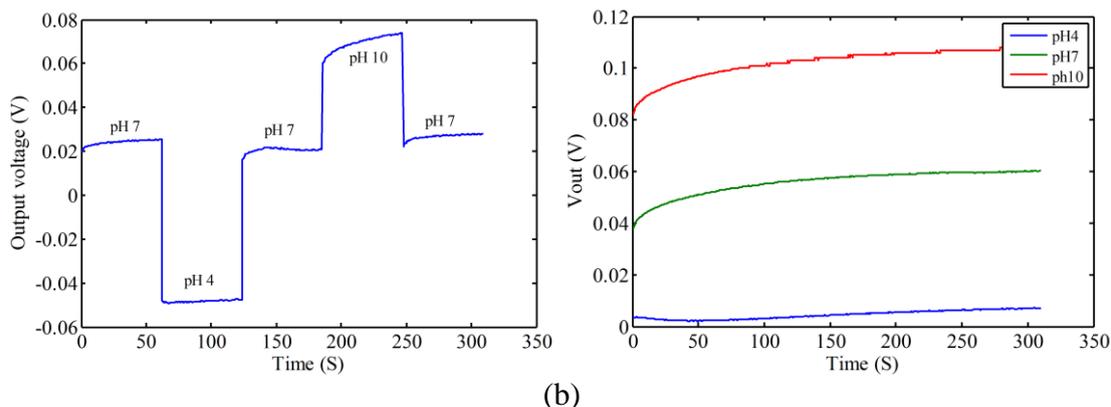


Figure 7. Hysteresis and drift at buffer solutions of pH (4, 7 and 10) under (a) light source (b) dark

Table 1. pH characteristics of sensitive membranes under different light conditions

Sensitive membrane	Under light source					In dark					Ref.
	Sensitivity (mV/pH)	Hysteresis (mV)	Drift ($\mu\text{V/s}$)			Sensitivity (mV/pH)	Hysteresis (mV)	Drift ($\mu\text{V/s}$)			
			pH4	pH7	pH10			pH4	pH7	pH10	
Si ₃ N ₄	28.3	-	-	-	-	50	1	4	10	40	[7]
CuS	19	5.2	21.7	155.8	90.4	23	2.66	13.1	73.5	85.8	This work

4. CONCLUSION

CuS thin film deposited by SPD on the glass substrate was used in this research as an extended gate for FET and exposed to XRD and FESEM measurements. Then the membrane used as pH sensor under two conditions; dark and high-intensity white light, after that the sensitivity, hysteresis and drift were measured for each case. It can be concluded from the results obtained in this research that the membrane was sensitive to light which affects the threshold voltage and generates the photocurrent, and the pH sensitivity was decreased when exposed to light. The sensitivity and the linearity had their minimum values under light source (19 mV/pH and 95.9%) while they were maximum in dark (23 mV/pH and 96.5%). The hysteresis (2.66 mV) and drift (13.1, 73.5 and 85.8 $\mu\text{V/s}$ for pH4, pH7 and pH10, respectively) in dark had minimum values which is the best behaviour of the membrane.

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