pH Sensing Characteristics of CuS/ZnO Thin Film Implemented as EGFET

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Abstract. Copper sulphide (CuS) is one of the most important semiconductor materials used in many applications for its semiconducting characteristics. CuS nanoscale thin films were deposited on various substrates using various methods of deposition; recently CuS thin films were used as extended gate field effect transistor (EGFET) and implemented as a pH sensor. In this work, CuS thin film was deposited on ZnO layer using spray pyrolysis deposition (SPD). CuS solution (0.4 M) was prepared from copper(II) chloride and sodium thiosulfate dissolved in deionised water. The precursors used to prepare CuS solution were copper chloride and sodium thiosulfate with 0.4 M concentration, and these precursors were solved using deionized water. The structural characteristics of this thin film show two phases for CuS; covellite and chalcocite with grain size of 31.2 nm. Nanoplate structure with a lot of aggregations was achieved from this deposition and it is confirmed by morphological examination, which estimates the roughness of the film to be 0.145 µm. CuS/ZnO thin film was used as EGFET and applied as pH sensor; the sensitivity and hysteresis were measured for this sensor to be 23.3 mV/pH and 17.5 mV, respectively.

1. Introduction

Determination of pH value was very necessary for a lot of biological and biochemical processes [1]. The ion-sensitive field-effect transistor (ISFET) was first proposed by Bergveld in 1970 in neurophysiological measurement [2]. An ISFET was modified to metal oxide field-effect transistor (MOSFET) which includes metal electrode gate [3], while in case of ISFET the reference electrode plays the role of the gate [4]. Furthermore, the MOSFET was alternated to extended gate field-effect transistor (EGFET) which is investigated by Spiegel et al. in 1983 [5] to isolate the FET from the chemical environment, EGFET can be described as the structure that contains chemically sensitive thin film at the end of the signal line which extended from the FET gate electrode [3]. The EGFET was distinguished from ISFET by many advantages such as; low cost, less insensitivity induced by temperature and light fluctuations, high shape flexibility of the extended gate structure, simpler to passive and package, better long-term stability [6], and disposable gate [7]. Furthermore, the method of using a disposable thin film enables the exchange of the sensing thin film when a chemical damage occurs, it will be easier than fabricating a new device [3].
The chemical reaction depends on the number of the surface sites per unit area (Ns) which is also called surface site density, according to the site-binding model [1].

The sensitivity parameter \( \beta \) was estimated using the equation [8] expressed below:

\[
\beta = \frac{2q^2N_s(K_a/K_b)^{1/2}}{kTCDL}
\]

where \( q \) is the electron charge, \( N_s \) represents the surface site density, \( K_a \) and \( K_b \) are the acidic and basic constants, respectively, \( k \) is the Boltzmann constant, \( T \) indicates the absolute temperature and \( CDL \) is the capacitance of the electrical double layer.

A lot of thin films of different materials were used to implement as a pH sensor, some of these materials which exhibit high pH sensitivity were PdO [9] and ZnO [6] thin films. Recently CuS thin films also implemented as pH sensors under various conditions and parameters [3, 10-12]. Due to the high sensitivity of ZnO sensor and good semiconducting characteristics of CuS material, the CuS/ZnO thin film was fabricated in this work to implement as pH sensor to modify the sensitivity of CuS sensor.

To the best knowledge of authors, there is no previous application for the CuS/ZnO as a pH sensor. In this work, the structural, morphological and sensing characteristics were studied, and the sensing mechanism was analyzed to highlight the main parameters which affect the pH sensor quality.

2. Methodology

2.1 Thin Film Synthesis

CuCl\(_2\).2H\(_2\)O (0.4 M) and Na\(_2\)S\(_2\)O\(_3\).5H\(_2\)O (0.4 M) were dissolved separately in deionized water using ultrasonic instrument. Then these two solutions were mixed at room temperature to form CuS solution (0.4 M), this solution was sprayed onto 100 nm thickness of ZnO layer (deposited by RF sputtering onto glass substrate) by using spray system. This system was used to synthesis CuS thin film in nanoscale; it is very simple and low-cost system to assemble. The substrate temperature used for deposition was fixed at 200 °C and the distance between substrate and airbrush nozzle was 30 cm, this distance was suitable for solvent evaporation and helps the chemical reaction to form the CuS nanoplate structure on the substrate. The spray rate was (1:1) s (ON: OFF) for 10 times then switch off the spray for 1 minute to keep the temperature of the substrate at the specified range, this cycle was repeated 6 times. Number of cycle was used to determine the thickness of thin film, after completing the process. The thin film was kept on the heater for about 1 hour to complete the growth of the nanostructure particles. The CuS/ZnO thin film was analysed to check its structural and morphological characteristics before the sample was being used as EGFET for pH sensing application.

2.2 Characterization Techniques

Phase purity and crystal structure were analysed by using PANalytical X-ray diffractometer (XRD) equipped with CuK\(\alpha\) source (\(\lambda=0.15418\) nm). Morphological observations were obtained by NOVA NANOSEM 450 field emission scanning electron microscopy (FESEM). Surface roughness of the thin films was examined by BRUKER, Dimension edge atomic force microscopy (AFM). And finally, for sensing measurements; pH sensitivity and hysteresis were measured using Keithley, Semiconductor Characterization System (2400-SCS).

2.3 pH Sensing and Hysteresis Systems

The system used to measure pH sensitivity of the CuS/ZnO thin film was sketched in Figure 1(a). It consists of two Keithley instruments; one was used to set the gate-source voltage (\(V_{gs}\)) at 3 V and measure the drain-source current (\(I_{ds}\)) response versus drain-source voltage (\(V_{ds}\)) for pH buffer solution (2, 4, 6, 8, 10 and 12), this measurement gives saturation regime. And the second Keithley instrument was used to set (\(V_{ds}\)) at 0.3 V and measure (\(I_{ds}\)) response versus (\(V_{gs}\)), the output curves formed the linear regime. The hysteresis was measured using the setup shown in Figure 1(b), this setup is working without
MOSFET and have only one Keithley instrument to find the potential difference between the reference electrode and the sensing thin film. The output signal can be expressed as [13]:

\[ V_{\text{OUT}} = V_{\text{IN}}^+ - V_{\text{IN}}^- = V_{\text{ERF}} - V_{\text{SENSING--FILM}} \]  

(2)

where \( V_{\text{IN}}^+ \) and \( V_{\text{IN}}^- \) are the two-input terminal voltage of the Keithley instrument, \( V_{\text{ERF}} \) and \( V_{\text{SENSING--FILM}} \) are the reference electrode voltage and the sensing film voltage, respectively. For this measurement, Keithley instrument was used as a voltmeter to measure the voltage difference between reference electrode and sensor surface at acidic, basic and neutral environment as the following sequence of pH (7-4-7-10-7). The hysteresis was measured by calculate the difference between the last value and first value of pH7.

![Figure 1: pH sensing and hysteresis systems](image)

3. Results and Discussion

3.1 Structural Analysis

Structural characteristics of CuS/ZnO thin film were characterised using X-ray diffractometer as shown in Figure 2. The XRD image illustrates that this film includes two phases of CuS; covellite CuS phase with orientations indexed as (103) and (206) and chalcocite CuS phase with single peak indexed as (002), with a hexagonal unit cell. Furthermore, there is a weak peak indexed as (002) belongs to ZnO material; among all these peaks and phases the covellite CuS phase is the dominant phase.

![Figure 2: XRD image of CuS/ZnO EGFET.](image)
The grain size was calculated from the Scherrer equation [14] as expressed below:

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

where \( \lambda \) is the wavelength of the CuK\( \alpha \) radiation, \( \beta \) is the FWHM in radius, and \( \theta \) is the Bragg angle. The average grain size of CuS nanoparticles was estimated to be 31.2 nm.

3.2 Morphological and Roughness Characteristics

FESEM image of CuS/ZnO thin film described the formation of nanoparticles on the surface of thin film, as illustrated in Figure 3. These nanoparticles include nanoplates and large amount of agglomerations, which is due to uneven heating on the substrate. The surface roughness of the CuS/ZnO thin film was measured using AFM to be 0.145 \( \mu \)m. The image of surface roughness was illustrated in Figure 4.

3.3 pH Sensitivity, Linearity and Hysteresis

Two regimes were obtained from the measurement using system shown in Figure 1. These regimes represent the response of drain current according to drain and gate voltages. The essential concept of pH sensor is the reaction between hydrogen ions available within the electrolyte and metal ions available on the sensor surface. This reaction leads to ion-exchange between electrolyte and sensor surface and that affects the gate charge, which is the sensor itself. Metal oxide could be hydrolyzed in the presence of water, forming hydroxide layers (M-OH) throughout its surface. Water molecules that available in the electrolyte could be adsorbed onto the sensor surface of the scattered oxide particles; the sensor surface may attract and adsorb additional layers of polar water molecules due to the polar hydroxyl groups (-OH). The oxide or hydroxide surface may be charged by reacting with H\(^+\) or OH\(^-\) ions according to the surface amphoteric reactions, which can be expressed in the following two equations [15]:

\[ M - OH + H^+ \leftrightarrow M - OH_2^+ \]  
\[ M - OH + OH^- \leftrightarrow M - O^- + H_2O \]
In acidic environment (high amount of H\(^+\) and less pH value), hydroxide sensor surface adsorbs protons [H\(^+\)] producing positive charge surface (\(M - OH^+_2\)). Whilst, in basic environment (high amount of OH\(^-\) and high pH value), the surface loses protons producing negative charge surface (\(M - O^-\)). The sensing process depends on these sites and the surface charge which were controlled by the pH of the solution [15]. Since the sensor is the extended gate of the MOSFET, then the positive charge accumulated on it causes increasing conduction channel (drain and source), which increase the current flow through this channel.

The relation between \(V_{gs}\) and pH value was plotted in Figure 5 to calculate the pH voltage sensitivity which is 23.3 mV/pH and linearity 96.1%. The hysteresis of the pH sensor indicates the delay in pH response due to the surface defect of the sensor, this defect belongs to the nanocrystals in the sensor surface or underneath the surface, low hysteresis value denotes the quality of the sensor surface [3]. The result of hysteresis measurement was shown in Figure 6, its value was estimated using Equation 2, to be 17.5 mV, which consider reasonable value compared to a-Si:H and a-WO\(_3\) sensors which have hysteresis of 17.9 and 26.0 mV, respectively [16, 17]. The sensitivity and hysteresis values of CuS/ZnO sensor and other pH sensors were listed in Table 1. As can be seen from the table, CuS/ZnO sensor provides good sensing characteristics compared to many other pH sensors. As obtained in the previous paper [18], the pH sensing characteristics for CuS thin film can be affected by the type of the substrate used, because the substrate can modify the structure and crystal orientation of the thin films. Glass, Si and tungsten substrates have been used in the previous paper [18], while in this paper, ZnO was used as a substrate and the pH sensing characteristics have been discussed for this type of substrate and its effect on the structure and crystal orientation.

![Figure 5: Sensitivity plot of CuS/ZnO EGFET.](image1)

![Figure 6: Hysteresis of CuS/ZnO EGFET.](image2)

| pH sensor          | Method of fabrication | pH solution range | pH voltage Sensitivity [mV/pH] | Linearity [%] | Hysteresis [mV] | Loop time [minute] | Ref. |
|--------------------|-----------------------|-------------------|-------------------------------|---------------|-----------------|-------------------|------|
| CZTSe              | Solution-based method | 4-10              | 9                             | -             | -               | -                 | [14] |
| CuS using (DIW:Et as solvent) | Spray pyrolysis deposition | 2-12              | 22.9                          | 93.8          | 23.75           | 5                 | [12] |
| CuS in dark        | Spray pyrolysis deposition | 2-12              | 23                            | 96.5          | 2.66            | 5                 | [11] |
4. Conclusion

CuS/ZnO thin film was deposited onto glass substrate using spray pyrolysis method at substrate temperature 200°C. XRD analysis exhibited two CuS phases; covellite CuS and chalcocite Cu$_2$S phases with weak peak of ZnO. The average grain size of these nanoparticles was 31.2 nm. FESEM and AFM results show difference in nanoplate’s diffusion on the surface with many agglomerations, the surface roughness was found to be 0.145 µm. The pH voltage sensitivity and linearity were calculated in this study to be 23.3 mV/pH and 96.1%, respectively. The hysteresis of this sensor which described the delay in pH response was 17.5 mV. These results were seemed to be reasonable to use CuS/ZnO thin film as a pH sensor compared to many various pH sensors.

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