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Annealing Effect on the EGFET Based pH Sensing Performance of Sol-gel Spin-coated CuO Thin Film

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ABSTRACT

In this study, the effect of annealing temperature on the extended gate field effect transistor (EGFET) for pH sensors of CuO thin film was investigated. The CuO thin films were deposited on an indium tin oxide (ITO) substrate using the sol-gel spin-coating method. The thin films were then annealed in air ambient at 200 to 500 °C for 30 minutes. The sensitivity and linearity of the sensing electrodes were determined in a pH range from pH 2, 4, 7, 10 and 12. The sensing electrode annealed at 400 °C showed the highest pH sensitivity of 47.3 mV/pH. It showed that the post-annealing process improved the sensing performance of the device. The morphology characteristic was characterized by field emission scanning electron microscopy (FESEM) and showed a porous structure as the annealing temperature increased, indicating that the porous film could be the sensing electrode of an EGFET pH sensor. The hysteresis of the sensing electrode was measured in buffer solutions prepared at pH 7, pH 4, pH 7, pH 10, and pH 7 to find its pH response delay. These findings indicated that sol-gel spin-coated CuO thin film can be considered a promising candidate for applications as an EGFET-pH sensor.

Keywords: Extended gate field effect transistor (EGFET), pH sensor, sol-gel spin-coated, CuO thin film, post-annealing process

1. INTRODUCTION

The pH sensors are useful for many applications including soil quality measurements in agriculture, healthcare, water quality, and clinical applications. pH measurements can be performed by different methods, i.e potentiometric, ion-sensitive field effect transistors, and conductometric. Among these, potentiometric is the most commonly used due to the easy fabrication method and has been used over a longer period [1]. Van der Spiegel et al. [2] proposed the extended gate field effect transistor (EGFET), a potentiometric-type pH sensing device to overcome ion-sensitive field-effect-transistor (ISFET) drawbacks such as inadequate long-term stability, a lack of insulation and encapsulation [3]. The EGFET-pH sensor consists of a metal-oxide-semiconductor field-effect transistor (MOSFET) and a sensing membrane. Different from ISFET, the sensing membrane of EGFET is directly exposed to a buffer solution while the MOSFET device is isolated. This configuration has certain benefits, including being less sensitive to light, having simpler packaging, being inexpensive, and being utilized frequently [4].

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Several metal oxides (MOx) with micro and nanostructures morphologies have been reported as the sensing electrode in EGFET-pH sensor, i.e TiO_2, SnO_2, RuO_2, ZnO, Ta_2O_5, IrO_2, and CuO due to their high degree of accuracy and great sensitivity to hydrogen ions [5]. However, few studies were carried out to investigate the pH sensing performance of CuO nanomaterials compared to other sensing membranes [5]. Thus, in this work, the CuO thin film as a sensing electrode for the EGFET-pH sensor was studied. Copper oxide (CuO) is a p-type semiconductor with a narrow bandgap of 1.2 eV, inexpensive and chemically stable. The interesting properties of CuO have been explored in numerous applications such as in electrochemical sensors [1], [6], gas sensors [7], and antimicrobial materials [8].

In this paper, the pH sensitivity of the sol-gel CuO EGFET-pH sensor was studied by varying the annealing temperature during the deposition process. The sensing electrode was deposited using the sol-gel spin-coating method due to its simplicity, low cost, and non-hazardous process for pure or multi-phase ceramic coatings with controllable compositions and microstructures [9]. The fabricated samples were characterized for their morphology structure, pH sensitivity, and hysteresis in buffer solutions in the range of pH 2, 4, 7, 10 and 12. The experimental results suggest that the annealing process affects the morphology structure (porous-like structure) and thus improves the sensing performance of our device.

2. MATERIAL AND METHODS

2.1 Fabrication of CuO Sensing Membrane

CuO thin films as sensing electrodes were deposited onto the ITO-coated substrate using the sol-gel spin-coating method. To remove any contaminants, the ITO substrates ($2x1cm^2$) were ultrasonically cleaned in methanol and deionized (DI) water using Hwashin Technology Powerson 405 ultrasonic cleaner. After 10 minutes, the cleaned substrates were dried using nitrogen gases. The CuO solution was prepared by dissolving copper acetate (precursor) in isopropyl alcohol. Then, diethanolamine and polyglycerol (PEG) were mixed into the solution and stirred for 300 rpm at room temperature. After 10 minutes, the solution was filtered to remove the precipitate of the solution. The solution was then deposited on an ITO-coated substrate with an area of $1x1cm^2$ using the spin-coating method. The spin-coater was set into 2 different phases; 10s for 1500 rpm (1st phase) and 50s for 3000 rpm (2nd phase). During the deposition process, the layer was formed by depositing 10 drops of solution using a pipette. The films were dried at 100 °C for 10 min using a thermal furnace to remove excess solvent from the film. Then, the films were annealed in air ambient at 200, 300, 400, and 500 °C.

2.2 EGFET Sensor: Measurement Setup

Figure 1shows the measurement of the EGFET-pH sensor using various pH buffers of pH 2, 4, 7, 10, and 12 obtained from Merck Chemicals. All electrical measurements were carried out using Keysight B1500A Semiconductor Device Analyzer. The sensing electrode was connected to the gate of a commercialized MOSFET (CD4007UBE) using copper (Cu) wire as shown in Figure 2. The Cu wire was located on a bare ITO surface using silver paste and packaged with epoxy resin. Both the sensing and reference electrodes were immersed into the buffer solution for 1 min for stabilization before the measurement was done. The morphology characteristic of the fabricated sensing electrode was characterized using field emission scanning electron microscopy (FESEM) (JEOL JSM 7600F) with an operating voltage of 5 kV and a magnification of x10,000.

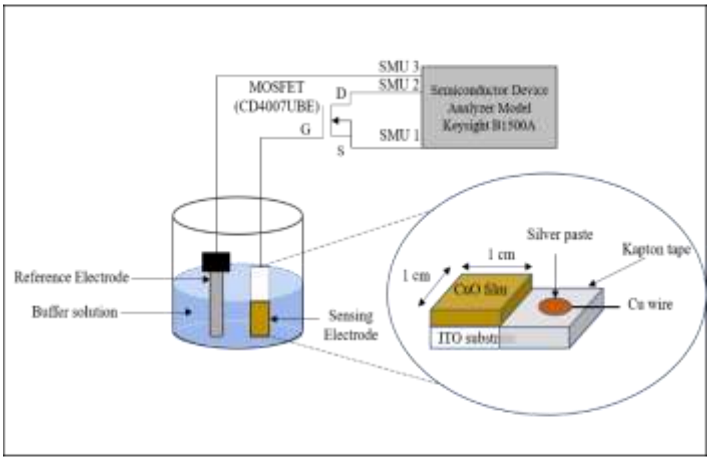

Figure 1. EGFET measurement setup.

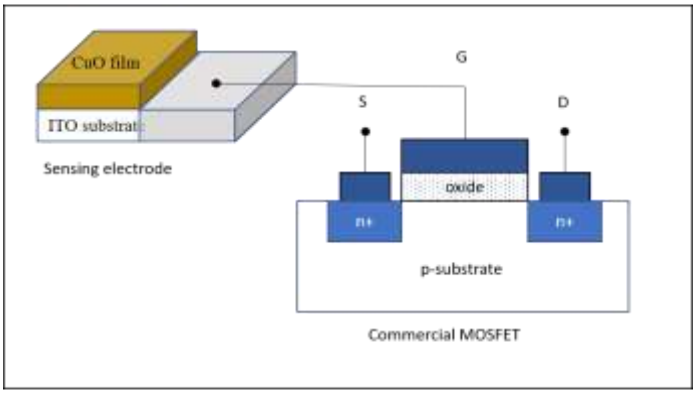

Figure 2. Schematic diagram of sensing structure.

3. RESULTS AND DISCUSSION

3.1 Structural Analysis

Figure 3 shows the FESEM images of the surface morphology of non-annealed and annealed CuO films in air ambient for 30 min at 200, 300, 400, and 500 °C. The inset in Figure 3 shows a magnified image of the film. A comparison between this sensing electrode was studied due to the differences in pH sensitivity which can be seen in Table 1. Several studies have shown that the annealing process may change the properties of the films, i.e morphology, roughness, particle size, and crystallinity which could affect device performance [9]–[11]. Thus, the morphology changes due to the annealing process can be observed as shown in Figure 3.

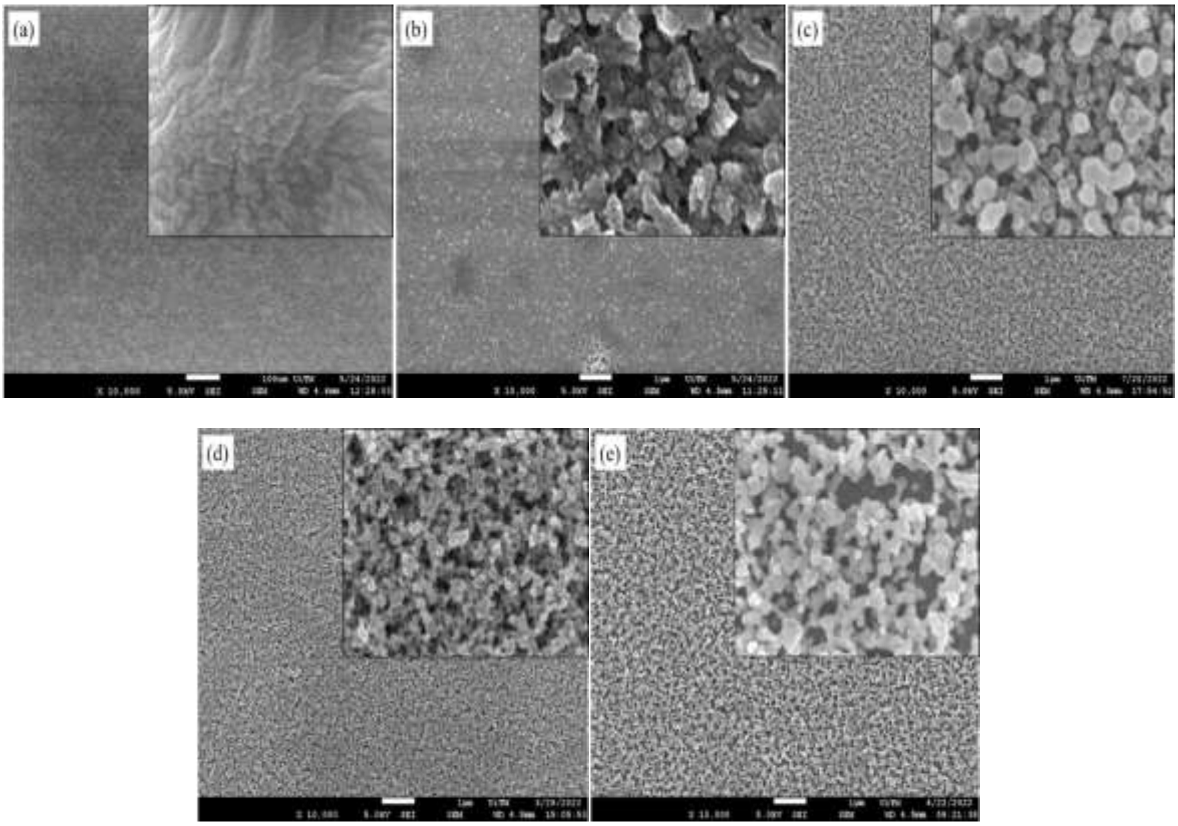

Figure 3. FESEM images and the locally magnified image (inset) of CuO films (a) non-annealed and annealed in air ambient for 30 min at (b) 200 (c) 300 (d) 400 and (e) 500 °C.

The non-annealed sensing electrode (Figure 3(a)) shows a smooth and dense film, meanwhile, the annealed sensing electrodes (Figure 3(b), (c), (d), and (e)) show a porous-like structure. As the annealing temperature was increased, these particles aggregated into irregular clusters on the film. The agglomeration of these clusters leads to the formation of larger grains and porosity of the film. As reported by Naif et al. [12] the porosity of the sensing electrode surface increases the effective adsorption surface by providing additional locations for ion reactions. As a result, the higher charge accumulation may enhance the sensor's sensitivity since as charges are accumulated, current increases.

3.2 Sensitivity and Linearity

The transfer characteristics (I_{DS} - V_{REF}) in the linear region for the CuO thin film was measured in the pH buffer solution ranging from pH 2, 4, 7, 10 and 12 with a reference voltage varied from 0 to 3 V. All sensing electrodes show similar behavior of transfer characteristic with a threshold voltage shifted to the right as the pH value increased (hydrogen ions concentration decreased). Noted that for an acidic solution, a small value of pH means that there is a high number of [H^+] ions, thus the voltage shows a small value. However, when the pH value becomes high for a basic solution (low [H^+] ions), the threshold voltage increases (shifted to the right) which is illustrated in Figure 4(a).

Figure 4(a) shows an example of a graph of I_{DS} - V_{REF} for a sensing electrode annealed at 400 °C. The pH sensitivity and linearity values were derived from the slope of I_{DS} - V_{REF} curves at I_{DS} = 100 μA as shown in Figure 4(b).

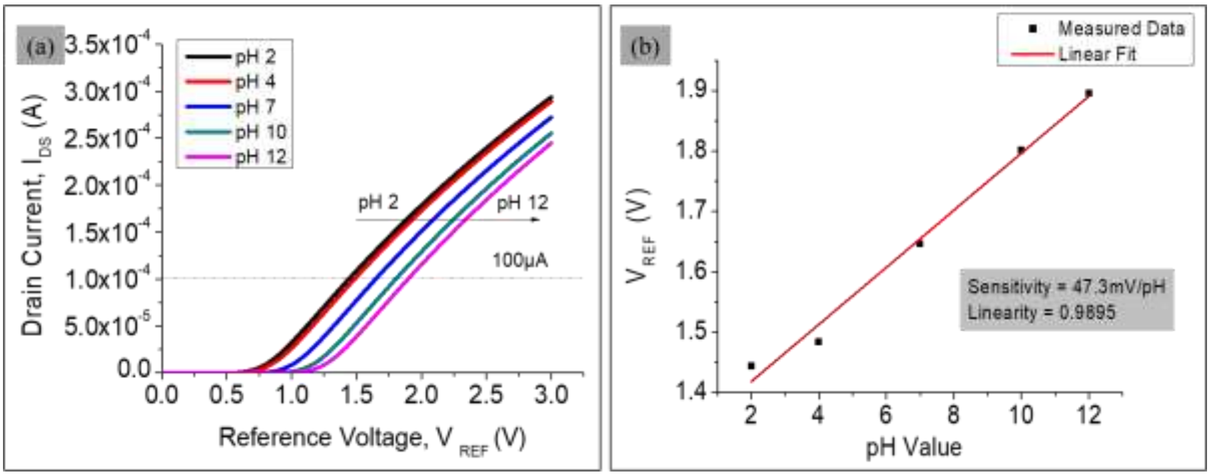

Figure 4. (a) Transfer characterististic (I_{DS} - V_{REF}) and (b) voltage sensitivity for the CuO EGFET-pH sensor annealed at 400 °C in the linear region for different pH values from pH 2 to 12.

The sensitivity and linearity values are tabulated in Table 1. It shows that the post-annealing process improves the sensing performance of sensing electrodes. The sensing electrode annealed at 400 °C gave the highest sensitivity of 47.3 mV/pH and linearity of 0.9895. However, the sensitivity declined to 44.5 mV/pH with linearity of 0.9734 as the sensing electrode annealed at 500 °C. Based on FESEM images in Figure 3, a porous-like structure was observed as the annealing temperature increased which might improve the sensitivity performance of our device. As reported by Cheng Chen et al. [13], this porous structure helps to enhance the wettability of an electrode which then creates a super-hydrophilic of sensing electrode for pH detection. However, the sensitivity deteriorates as the annealing temperature increases even though the porous structure is more significant for the sensing electrode annealed at 500 °C. This suggests that although the porosity of the film due to the annealing process would enhance the sensitivity, the optimized annealing temperature of CuO film is found to be at 400 °C. There is a possibility that the high temperature of the annealing process might affect the properties of the thin films, thus reducing the hydrophilic sites for H^+ and leading to decreased sensitivity.

Table 1 Sensitivity and linearity of CuO films annealed at various temperatures in air ambient for 30 min (linear region)

Annealing temperature (°C)	Sensitivity (mV/pH)	Linearity
As-deposited	25.3	0.9918
200	27.5	0.9528
300	44.4	0.9455
400	47.3	0.9895
500	44.5	0.9734

The following redox processes can be used to describe the pH-sensing mechanism of CuO thin film [14]:

$$CuO + 2H^+ \rightarrow Cu^{2+} + H_2O \quad (1)$$

$$Cu^{2+} + 2OH^- \rightarrow CuO + H_2O \quad (2)$$

Generally, the metal oxide surface consists of hydroxyl groups, which, when submerged in a solution, can either donate or receive a proton, leaving a net positively or negatively charged surface. The pH detection mechanism is depending on potential determining ions (PDI). This PDI can be either hydrogen (H^+) or hydroxyl (OH^-) ions. The hydroxyl group will be protonated in an acidic solution as shown in Equation (1) and deprotonate ions in an alkaline solution (Equation (2)) that result in positively or negatively charged on the surface of the sensing layer [15].

According to the site binding model, the surface voltage of an oxide layer fluctuates with the pH of an electrolyte solution. The surface potential voltage (Ψ_o) between the sensing layer and the electrolyte interface can be expressed as [5], [16]:

$$2.303\left(pH_{pzc} - pH\right) = \frac{q\Psi_o}{kT} + sinh^{-1}\left(\frac{q\Psi_o}{kT}\cdot\frac{1}{\beta}\right) \tag{3}$$

where the pH_{pzc} is the pH value at the point of zero charges, k is the Boltzmann constant, q is the electron charge, β is the sensitivity parameter and T is the absolute temperature.

Since the sensing electrode annealed at 400 °C shows the highest sensitivity among others, the sensing performance (current sensitivity and hysteresis) of this sensing electrode was investigated. The pH current sensitivity of the sensing electrode was 0.9656 $(\mu A)^{1/2}$/pH with a linearity of 0.9909 and the values of I_{DS} were chosen at a constant V_{DS} = 2 V. Figure 5(b) was obtained from the graph of $I_{DS} - V_{DS}$ curves in buffer solutions ranging from pH 2, 4, 7, 10 and 12 when MOSFET was operating in the saturation region at V_{REF} of 2 V. In this case (saturation region), a channel has been created, enabling the passage of current between the source and the drain. It can be seen that the I_{DS} -V_{DS} curve (Figure 5(a)) shifts downward with an increase in pH values.

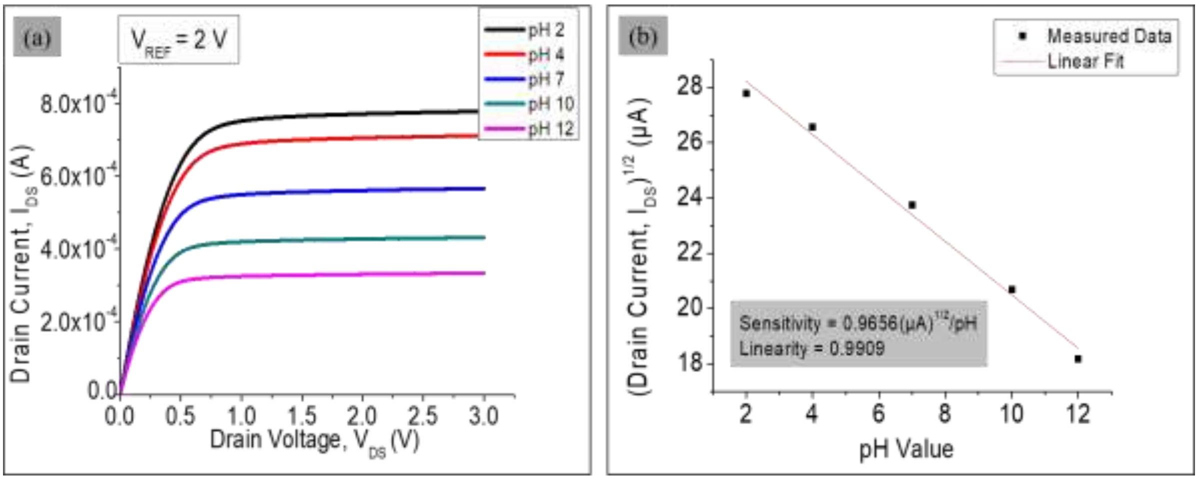

Figure 5. (a) Output characteristic (I_{DS} - V_{DS}) and (b) current sensitivity for the CuO EGFET-pH sensor annealed at 400 °C in the linear region for different pH values from 2 to 12.

3.3 Hysteresis

Figure 6 shows the hysteresis characteristic of the sensing electrode annealed at 400 °C. Hysteresis is defined as a delay in pH response. This is due to the ions in an electrolyte interacting chemically with slow-reacting surface sites underneath the membrane surface and/or membrane surface defects [17]. The pH sensor performs substantially better when the hysteresis value is low because it denotes a very low defect density on the sensing electrode surface and causes the pH sensor to perform with less delay performance.

The hysteresis characteristic was measured using the I_{DS} – V_{REF} curves for each pH value when the CuO sensing electrode was immersed in alternating cycles of pH buffer solutions i.e., pH 7→4→7→10→7 for 5 min. The V_{REF} values were extracted for each pH solution at a fixed I_{DS} of 100 µA. The net hysteresis was calculated as a difference between the initial reference voltage and final reference voltage at pH 7 to be 45 mV. Accordingly, the hysteresis effect for this sensing electrode is quite high than other sensing electrodes reported elsewhere [12], [15], [18]. However, our device is still considered to be used as a pH sensor and further studies need to be done.

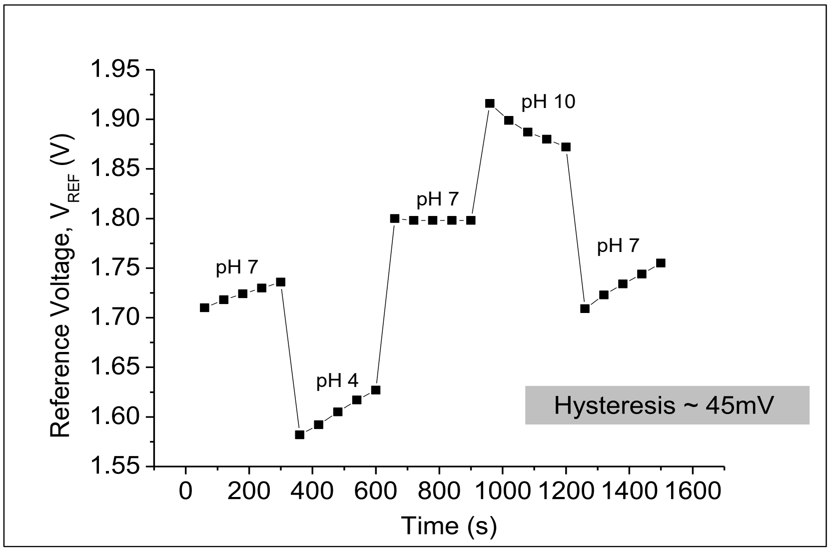

Figure 6. Hysteresis characteristic of the sensing electrode annealed at 400 °C in a pH loop of 7→4→7→10→7 over 25 min.

Table 2 shows the comparison of CuO and various sensing electrodes for EGFET-pH sensors based on sensitivity and fabrication methods. It can be seen that the sensitivity value of the CuO sensing electrode obtained in our work is comparable to other literature and yet a simpler fabrication method was used. As suggested by Libu Manjakkal et al. [5], the sensitivity value has always been influenced by fabrication methods and material composition as well. Both factors affect the microstructure, crystalline structure, particle shape, size, porosity, and morphology of MOx nanostructures (e.g thin film, nanowires, nanotubes, nanorods, etc). As an example, Cheng Chen et al. [13] have reported that a porous surface of the thin film helps to improve pH sensitivity. Sol-gel is one of the methods that can generate high porosity and increases the substrate surface area. The fabrication parameters of the sol-gel method such as spin speed, annealing process, and precursor solution can be tuned to improve the properties of thin film to be used as a sensing electrode. Thus, in this work, the effect of the annealing process on the sensing electrode was studied. The experimental findings suggest that the sensitivity is affected by the properties of the films (changes of morphology structure) due to the annealing process.

Table 2 Comparison of CuO based EGFET-pH sensor and various sensing electrodes.

Sensing electrode	Fabrication method	Sensitivity (mV/pH)	Hysteresis	Ref
TiO_2 thin film	Sol-gel	58.7	86.17	[15]
PdO thin film	Reactive electron beam evaporation and thermal oxidation	62.87	7.9	[19]
CuS thin film	Spray pyrolysis	27.8	11.4	[10]
PSi thin film	Anodization	66	8.2 10.5	[12]
CuO nanoflower	Simple low-temperature chemical bath method	-28	-	[1]
CuO nanowire	Thermally annealing of Cu film at 450 ∘C for 5 h in air	18.4	-	[16]
CuO nanoparticle	Hydrothermal	60	-	[20]
CuO thin film	Sol-gel	47.3	45	This work

4. CONCLUSION

In this work, CuO as sensing electrodes were prepared by the sol-gel spin-coating method. The effect of annealing temperature was varied at 200, 300, 400, and 500 °C for 30 minutes in air ambient. These CuO thin films were tested for pH sensors using the EGFET technique in a pH buffer solution ranging from pH 2, 4, 7, 10 and 12. The sensing electrodes were characterized for their surface morphology using FESEM. From the FESEM image, the sensing electrode shows a dense morphology structure at a lower annealing temperature. However, as the annealing temperature increased, a porous-like structure was observed for the sensing electrode annealed at high temperatures. It is noticeable that the surface morphology could be affected by changing the annealing temperature, thus varying the pH sensitivity. The sensitivity and linearity of the sensing electrodes in the linear region were calculated based on the slope of the transfer characteristic (I_{DS} - V_{REF}). It was found that the sensitivity in the linear region increased with annealing temperature until maximum values of 47.3 mV/pH and linearity of 0.9895 were attained for the sample annealed at 400 °C. Based on the highest sensitivity performance (sample annealed at 400 °C), the sample was measured in the saturation region which gave a current sensitivity of 0.9656 $(\mu A)^{1/2}$/pH and linearity of 0.9909. To find its pH delay response, the hysteresis measurement was done by immersing the sample in pH 7→4→7→10→7 for 5 minutes in each pH buffer solution. The hysteresis value was found to be 45 mV. The obtained results suggest that the porosity of the films due to the annealing temperature affects the sensitivity of our device. The characteristic and properties of the sensing electrode in this work is suitable to be applied as a pH sensor.

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REFERENCES

[1] S. Zaman, M.H. Asif, A. Zainelabdin, G. Amin, O. Nur, and M. Willander, CuO nanoflowers as an electrochemical pH sensor and the effect of pH on the growth, J. Electroanal. Chem., vol 662, no. 2, pp. 421–425, 2011.

[2] J. van der Spiegel, I. Lauks, P. Chan, and D. Babic, The Extended Gate Chemically Sensitive Field Effect Transistor As Multi-species Microprobe, Sensors and Actuators, vol 4, pp. 291–298, 1983.

[3] B.E. Alvarez-Serna and R.G. Ramírez-Chavarriá, EGFET-based pH Sensor Coupled with Low-cost Electrochemical Screen-printed Electrodes, J. Phys. Conf. Ser., vol 1723, no. 012024, pp. 1–6, 2021.

[4] F.A. Sabah, N.M. Ahmed, Z. Hassan, and M. Abdullah Almessiere, Influences of substrate type on the pH sensitivity of CuS thin films EGFET prepared by spray pyrolysis deposition, Mater. Sci. Semicond. Process., vol 63, pp. 269–278, 2017.

[5] L. Manjakkal, D. Szwagierczak, and R. Dahiya, Metal oxides based electrochemical pH sensors: Current progress and future perspectives, Prog. Mater. Sci., vol 109, p. 100635, 2020.

[6] L. Manjakkal, B. Sakthivel, N. Gopalakrishnan, and R. Dahiya, Printed flexible electrochemical pH sensors based on CuO nanorods, Sensors Actuators, B Chem., vol 263, pp. 50–58, 2018.

[7] F. Peng et al., Studies on sensing properties and mechanism of Cuo nanoparticles to H_2S gas, Nanomaterials, vol 10, no. 4, pp. 1–14, 2020.

[8] K. Mageshwari and R. Sathyamoorthy, Flower-shaped CuO Nanostructures: Synthesis, Characterization and Antimicrobial Activity, J. Mater. Sci. Technol., vol 29, no. 10, pp. 909–914, 2013.

[9] P.C. Yao, M.C. Lee, and J.L. Chiang, Annealing effect of sol-gel TiO_2 thin film on pH-EGFET sensor, in Proc. - 2014 Int. Symp. Comput. Consum. Control. IS3C (2014) pp. 577–580.

[10] F.A. Sabah, N.M. Ahmed, Z. Hassan, and M.A. Almessiere, Influence of CuS membrane annealing time on the sensitivity of EGFET pH sensor, Mater. Sci. Semicond. Process., vol 71, pp. 217–225, 2017.

[11] A.B. Rosli, Z. Awang, S.S. Shariffudin, and S.H. Herman, Annealing Temperature Dependence of ZnO Nanostructures Grown by Facile Chemical Bath Deposition for EGFET pH Sensors, IOP Conf. Ser. Mater. Sci. Eng., vol 340, no. 1, pp. 1–8, 2018.

[12] N.H. Al-Hardan et al., High sensitivity pH sensor based on porous silicon (PSi) extended gate field-effect transistor, Sensors, vol 16, no. 6, pp. 1–12, 2016.

[13] C. Chen, Y. Zhang, H. Gao, K. Xu, and X. Zhang, Fabrication of Functional Super-Hydrophilic TiO_2 Thin Film for pH Detection, chemosensors, vol 10, no. 182, pp. 1–15, 2022.

[14] X. Wang, L. Sun, T. Wang, and Y. Shi, Temperature-Compensated pH Microelectrode Array Sensors Based on Copper-Oxide/Polyaniline Modification, IEEE Sens. J., vol 20, no. 24, pp. 14598–14606, 2020.

[15] M. Al Hadi Zulkefle et al., Evaluation on the EGFET pH sensing performance of sol-gel spin coated titanium dioxide thin film, J. Teknol., vol 83, no. 4, pp. 119–125, 2021.

[16] S.P. Chang and T.H. Yang, Sensing performance of EGFET pH sensors with CuO nanowires fabricated on glass substrate, Int. J. Electrochem. Sci., vol 7, no. 6, pp. 5020–5027, 2012.

[17] L. Bousse, S. Mostarshed, B. van der Schoot, and N.F. de Rooij, Comparison of the hysteresis of Ta_2O_5 and Si_3N_4 pH-sensing insulators, Sensors Actuators B. Chem., vol 17, no. 2, pp. 157–164, 1994.

[18] T.M. Pan, C.H. Lin, and S.T. Pang, Structural and Sensing Characteristics of NiOx Sensing Films for Extended-Gate Field-Effect Transistor pH Sensors, IEEE Sens. J., vol 21, no. 3, pp. 2597–2603, 2021.

[19] A. Das, D. Hsu, C. Chen, L. Chang, and C. Lai, Highly sensitive palladium oxide thin film extended gate FETs as pH sensor Sensors and Actuators : Chemical Highly sensitive palladium oxide thin film extended gate FETs as pH sensor, Sensors Actuators B. Chem., vol 205, pp. 199–205, 2014.

[20] S.M. Toma, J. Mistry, M.A. Yousuf, and M. Jamal, Development of copper oxide based solid state pH sensor, in 4th International Conference on Civil Engineering for Sustainable Development (2018), pp. 1–8.