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Sensing Performance of EGFET pH Sensors with Zinc Oxide (ZnO) Nanowires

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Abstract

Zinc Oxide (ZnO) was deposited by Spray Pyrolysis Technique on the Ti/Pt sputtered substrate and was used as a pH sensor in Extended Gate Field effect transistor (EGFET) devices. The pH sensor was connected to a commercial MOSFET (CD4007UB). ZnO nanorods were prepared by spray of aqueous solutions containing Zinc Chloride ($ZnCl_2$) and thiourea (tu) at different molar ratios (1:0, 1:0.25) and at constant temperature (520°C). Obtained layers by Spray Pyrolysis Technique were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectrometry (EDS), Dektak Profilometer and Atomic Force Microscopy (AFM).Small addition of thiourea into $ZnCl_2$ solution ($ZnCl_2$: tu = 1:0.25) supports development of significantly thinner ZnO nanorods with higher aspect ratio compared to those obtained from $ZnCl_2$ solution. The current sensitivity results showed a much greater sensitivity for the sample with $ZnCl_2$ and thiourea than the sample obtained only by $ZnCl_2$.

Key words- EGFET, Nanowires, pH, ZnO

I. INTRODUCTION

Recently there is an increase in various modern diseases owing to irregular health. The pH value of blood is an important factor of the human body and even a small change in the pH of body fluids can pose a problem. Therefore, pH sensors play an important role in many clinical applications such as environmental monitors, blood monitors, biological and chemical analyses. [1-3]Semiconductor-based sensors have attracted a lot of interest and Field Effect Transistor (FET) based devices have been

widely used in bio sensors [4, 5].Among such FET-based biosensors, several papers have demonstrated the fabrication of Ion-Sensitive Field Effect Transistor (ISFET) by using a standard MOSFET configuration where the gate is replaced by a sensing material that is directly exposed to the target solution [6]. An improvement in the configuration of this device was introduced by J. Van Der Spiegel et al, called Extended-gate Field effect transistors (EGFET). [7] EGFETs possess many advantages such as easy fabrication, small influence of optical illumination and operation temperature, and disposable gas. The EGFET consists of two parts: the sensing membrane structure and Metal-Oxide-Semiconductor FET (MOSFET) structure. The sensing membrane is externally connected to the gate of the commercial MOSFET so that only a part of the membrane is inserted in the solution while the MOSFET is preserved for reutilization. Recently, several materials have been widely used as the sensing membrane in EGFET pH sensors [8-10]. Among them, ZnO is a promising material membrane owing to their range of electrical and optical properties [11].

In this work we show the results obtained using Spray Pyrolysis where ZnO NWs were used as EGFET for pH sensing.

II. EXPERIMENTAL

The device is separated in two parts. The sensitive part is made of ZnO film deposited on a Ti/Pt sputtered (DC sputtering) glass substrate. The setup is completed by using a commercial CD4007UB MOSFET.

*A. **Fabrication of ZnO EGFET pH sensor***

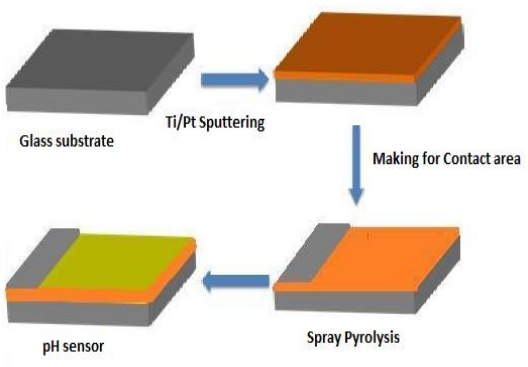


Figure 1: Pictorial depiction of pH sensor fabrication

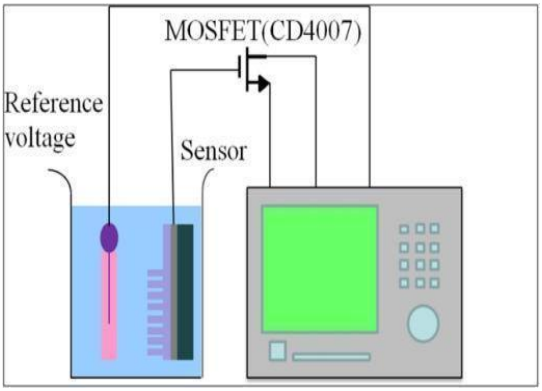


Figure 2: The EGFET as pH sensor setup

For the fabrication of EGFET sensors, before growing the ZnO NWs, glass substrates were cleaned with Ultrasonic Cleaner for 10 minutes. A 10nm/100nm thick Ti/Pt layer was first deposited onto the glass substrate by DC Sputtering to serve as a conducting layer. ZnO NWs were deposited using Spray Pyrolysis Technique. Spray aqueous solution was prepared by mixing of $ZnCl_2$ and thiocarbamide (tu) at the

molar ratios (Zn:tu) of 1:0 ($ZnCl_2$ solution without tu) and 1:0.25.The ZnCl2 concentration in solutions was adjusted to 0.1mol/L. The resultant solution in amount of 100ml was then sprayed. The deposition temperature was kept constant at 520ºC and controlled using an electronic temperature controller. The solution flow rate and gas pressure were kept constant. Air was used as the carrier gas supplied by filter equipped oil-free compressor. The procedure used to grow the ZnO NWs is schematically shown in Fig 1.

B. Measurement System

The device structure was constructed by connecting the sensing membrane to a commercial MOSFET as shown in Figure 2. The electric contact with the gate of the MOSFET was established. The electrode containing the film and the Ag/AgCl reference electrode were dipped in the buffer solution (pH value ranging from 4 to 10). In order to achieve solutions of various pH concentrations, pH capsules of 4, 9 and 13 along with hydrochloric acid and the sodium hydroxide was used to obtain the desired buffer solution. The electrical response of the pH sensors was measured using solutions of different pH values and the curves were obtained using an Agilent B1500A semiconductor device analyzer.

III. RESULTS AND DISCUSSIONS

The XRD data confirms the ZnO nanostructure growth (not shown). Figure 3(a) shows cross-sectional and top-view scanning electron microscopy (SEM) images for sample 1. Figure 3(b) shows the SEM images of Sample 2.From the figure 3(a),(b) it is seen that the Sample 2 with additive tu has enhanced growth of ZnO NW as compared to Sample 1.The AFM images of both the samples are as seen in Figure 4 (a),4(b).

From the line roughness data, it is clearly observed that the Sample 1 (45.351nm) is smoother than to Sample 2 (58.064). EDAX Figure 5(a) and 5(b) the material composition of the sample have been determined.

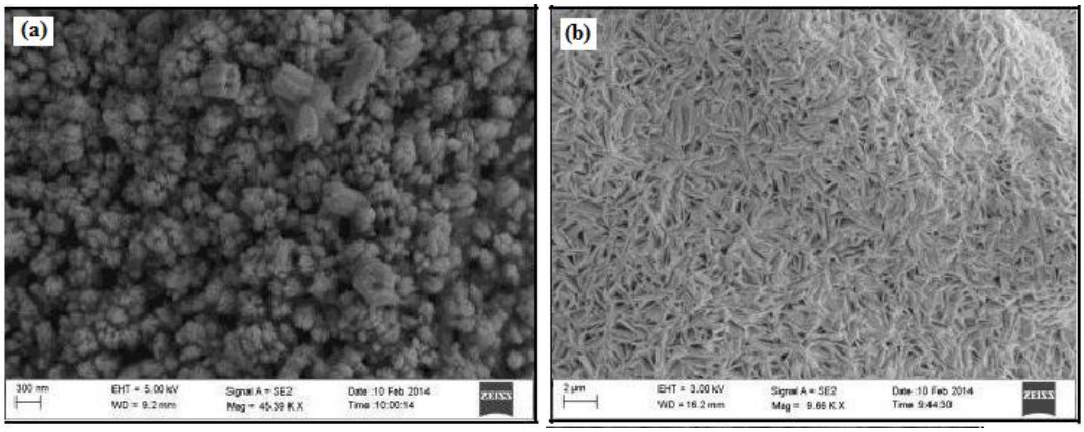


Figure 3: SEM image for (a) Sample 1 with $ZnCl_2$: tu (1:0) (b) Sample 2 with $ZnCl_2$: tu (1:0.25)

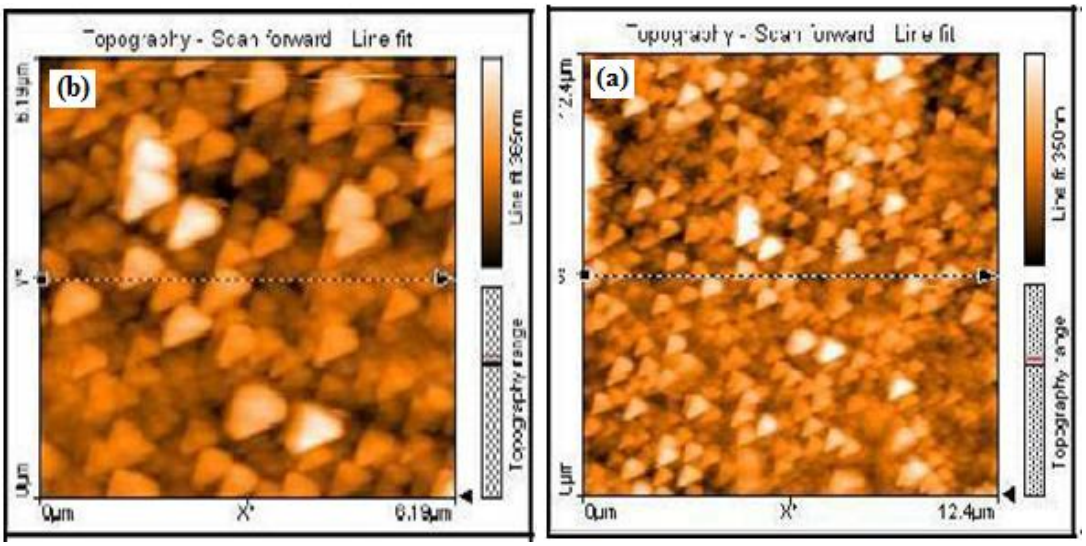


Figure 4: AFM image of (a) sample 1 ZnO NWs at 6.14µm (b) sample 2 ZnO NWs at 12.4µm

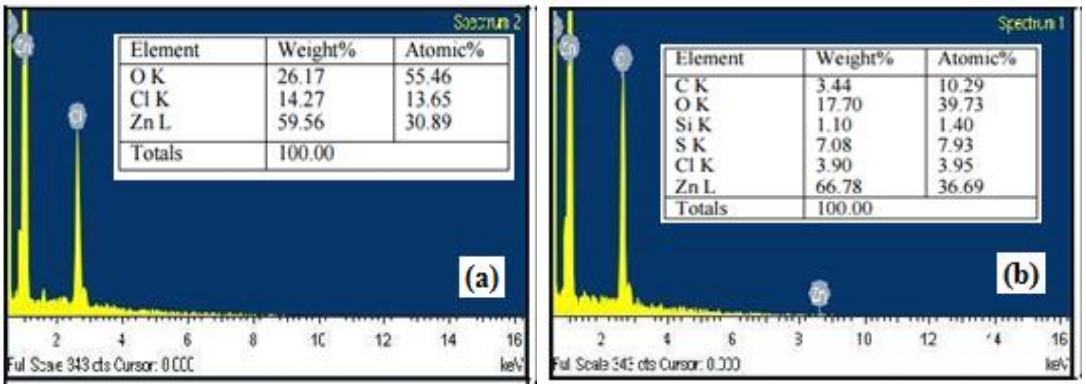


Figure 5: EDAX results showing the material composition of (a) Sample 1 (b) Sample 2

Sensor Mechanism:

At the oxide-water interface, water adsorption and dissociation occurs leading to the formation of surface hydroxyl groups, which are known to exhibit acid or basic properties, thus affecting the surface charge, Which are indcaters of PH. The Iso Electric Point (IEP) is the pH value, leading to a neutral charge. The protonation or deprotonation mechanism in aqueous medium, as shown in Scheme 1, occurs with metal oxides in general as they experience pH variation. [12]

a) pH < IEP b) pH = IEP c) pH > IEP

$$M\text{-}OH_2^+ \rightleftharpoons M\text{-}OH + H^+ \rightleftharpoons M\text{-}O^- + 2H^+$$

Increasing pH

Scheme 1: Reaction mechanism in an oxide-water interface

For pH< IEP, hydration of the outermost oxide layers cause a positive surface charge.

For pH= IEP, a neutral surface is obtained.

For pH> IEP, deprotonation of the surface film causes a negative charge.

Our samples are showing negative which indicates that ZnO is deteroid. The experimental results showed that Ids decreased with an increase in the pH value of the buffer solution. This is due to the deprotonation of the oxide upon increase in pH.

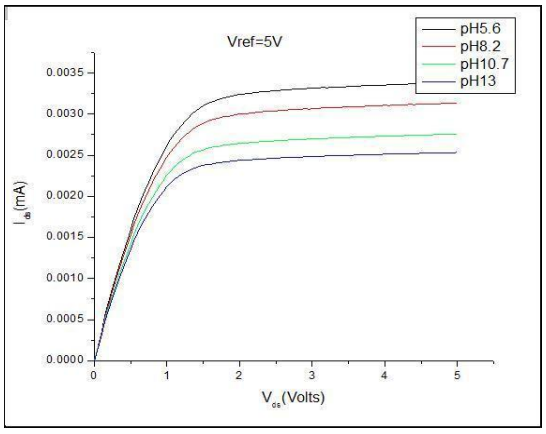


Figure 6: Ids-Vds characteristic of a pH sensor under

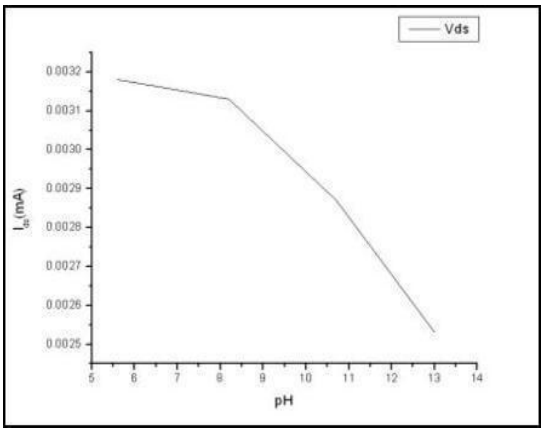


Figure 7: Ids-pH characteristics for Sample 1 different pH values

Thus, the hypothesis seems to be confirmed by the shape of the curve as shown in Figure 6. Moreover, the larger the pH value, the faster the decay due to more OH- ions. Based on the results shown in Fig. 6, the measured drain-source current as a function of pH value is shown in Fig. 7 and 9. During these experiments, Vds and Vref were kept constant. The current sensitivity was calculated from the linear relation between the drain-source current and the pH value. The sensing sensitivity of the pH sensors with ZnO NWs for Sample 1 was 94.89**µA/pH.** Similarly, the Ids-Vds characteristic along with the current sensitivity for Sample 2 is as shown in Figs. 8. The linear decrease in Ids-pH graph is due to the deprotonation state achieved for higher pH values.

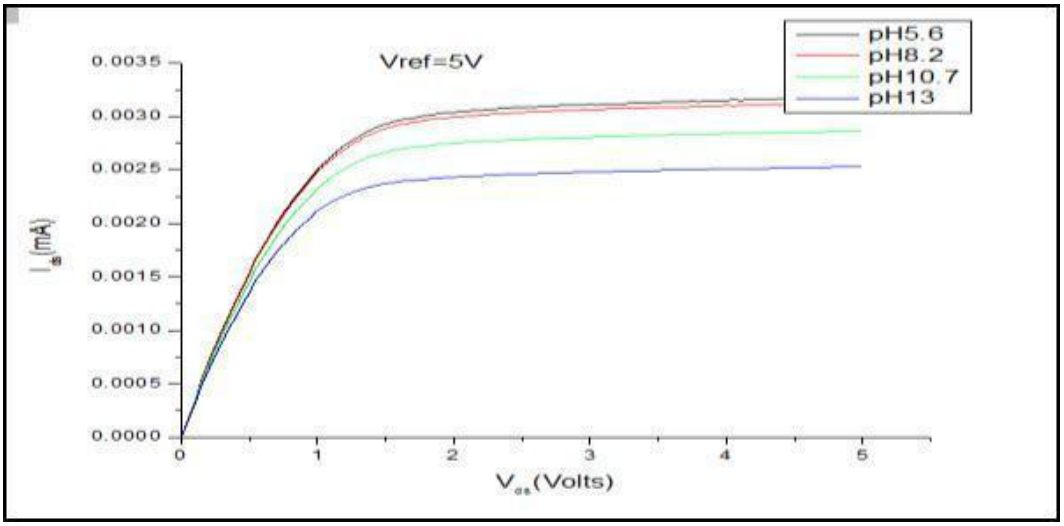


Figure 8: Ids-Vds characteristics for Sample 2

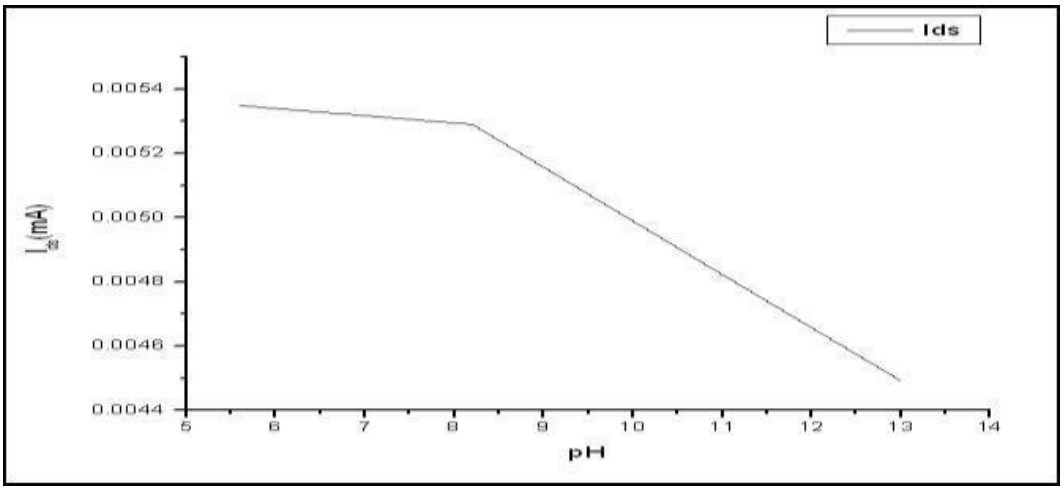
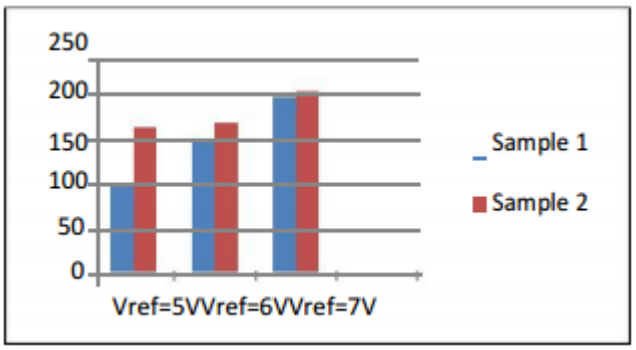


Figure 9: Ids-pH characteristics for Sample 2

From the Figure 9, it is observed that with the increase in pH, the Ids decreases. The current sensitivity for Sample 2 is calculated to be 158.605**µA/pH.** Therefore, we can conclude that the current sensitivity for Sample 2 is more than that as compared to Sample 1 for different Vref as shown in the Graph 1.



Graph 1: Current sensitivity comparison

IV. **CONCLUSION**

In this study, we have reported the synthesis of ZnO NWs by Spray pyrolysis Technique. The material characterization results indicate that Sample 2, with thiourea additive is the preferred sample. Electrical characterization performed on the pH sensor showed a decrease in Ids with increase in pH values for both the samples. The current sensitivity achieved by ZnO for Sample 2 was158.605 **µA/pH,** much more than that of Sample 1 with current sensitivity of **94.89µA**/pH.The response of the system was limited to pH values above 5 and below this value, the material showed negative results. The experimental results indicated that the ZnO-pH-EGFET sensor is a useful and successful device for higher pH sensing. Therefore, ZnO NW sensors can indeed demonstrate a good performance for application in pH sensing.

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