Annealing Temperature Dependence of ZnO Nanostructures Grown by Facile Chemical Bath Deposition for EGFET pH Sensors

Aimi Bazilah Rosli¹,², Zaiki Awang³, Shafinaz Sobihana Shariffudin¹ and Sukreen Hana Herman¹,²,³

¹NANO-ElecTronic Centre, Faculty of Electrical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.
²Integrated Sensors Research Group, Faculty of Electrical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.
³Microwave Research Institute, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.

Corresponding author: hana1617@salam.uitm.edu.my

Abstract. Zinc Oxide (ZnO) nanostructures were deposited using chemical bath deposition (CBD) technique in water bath at 95 °C for 4 h. Post-deposition heat treatment in air ambient at various temperature ranging from 200-600 °C for 30 min was applied in order to enhance the electrical properties of ZnO nanostructures as the sensing membrane of extended-gate field effect transistor (EGFET) pH sensor. The as-deposited sample was prepared for comparison. The samples were characterized in terms of physical and sensing properties. FESEM images showed that scattered ZnO nanorods were formed for the as-deposited sample, and the morphology of the ZnO nanorods changed to ZnO nanoflowers when the heat treatment was applied from 200-600 °C. For sensing properties, the samples heated at 300 °C showed the higher sensitivity which was 39.9 mV/pH with the linearity of 0.9792. The sensing properties was increased with the increasing annealing treatment temperature up to 300 °C before decreased drastically.

1. Introduction
pH plays a critical role in regulating the reactivity of many chemical species, thus its measurement is fundamental in many fields such as environmental science, agriculture, chemical engineering, chemistry, food science, biology and medicine. Field Effect Transistor (FET) based devices have attracted a lot interest in pH sensors field. Ion-sensitive field-effect transistor (ISFET) is one of FET biosensors that was introduced by Bergveld in 1970 [1-3]. The ISFET used a standard MOSFET configuration except that the gate was replaced with sensing membrane that was directly exposed to the solution [4-6]. This configuration induced device instability and also low current sensitivity of ISFET [7]. In 1983, extended gate field-effect transistor (EGFET) was proposed by Van der Spiegel et al to overcome the disadvantages of ISFET. EGFET is a structure used to isolate FET from the chemical environment [4, 8] in which, a chemically sensitive membrane is connected at the end of the signal line extended from the FET gate electrode [9]. EGFET has many advantages compared to ISFET, including insensitivity to light, simplicity of passivation and packaging [10-12]. EGFET uses the same principle...
of operation of the ISFET with the principal distinction between pH-ISFET and pH-EGFET sensors is the impedance of sensing films [11]. Metal oxide semiconductors have attracted considerable attention as the EGFET sensing membranes due to their high sensitivity, fast response and recovery, low detection limits and low fabrication cost as sensors [13-15]. At present, ZnO, SnO$_2$ and TiO$_2$ have been found to be prominent sensing materials by scientific community [14, 16, 17]. Among these materials, extensive studies on the ZnO have been done for various applications due to its excellent properties in terms of electrical and optical [18, 19] properties. Besides that, ZnO also exhibits various types of morphology such as nanorods, nanowire, tetrapods and nanocombs [20-23]. These nanostructures were reported to increase the sensitivity of sensors due to its high surface to volume ratio that leads to high surface area for sensor activity [24]. Various methods have been developed to attain various structures of ZnO such as RF sputtering, thermal chemical vapor (TCVD), hydrothermal and sol-gel process [11, 25-27]. Among these methodology, the solution-based process is favorable due to its low cost, flexibility when it comes to tuning the reaction parameters, and easy to handle[28, 29].

In this work, the ZnO nanostructures was deposited using simple chemical bath deposition (CBD) process in water bath at 95 °C for 30 min. The post-deposition heat treatment temperature was varied from 200 to 600 °C to study the effect of annealing temperature on ZnO nanostructures as EGFET pH sensors.

2. Experimental details

2.1. ZnO Nanostructures Deposition
The ZnO nanostructures were grown by simple the chemical bath deposition process. For the solution preparation, 0.23 g zinc nitrate hexahydrate [Zn (NO$_3$)$_2$. 6H$_2$O] was mixed with 0.11 g of hexamethylenetetramine (C$_6$H$_{12}$N$_4$) in 100 ml of deionized water. Then, the mixture was stirred on hot plate at 300 rpm for 3 hours at room temperature to ensure well dispersion. After that, the mixture was transferred into a water bath with the constant temperature 95 °C for 4 hours followed by a 14-hours cooling process at room temperature. Then, the sample was rinsed with deionized (DI) water to remove the unused salt. After the drying process, the samples were annealed in at the temperature ranging from 200 to 600 °C for 30 min. As-deposited sample was also prepared as comparison.

2.2. Sample Characterization
The surface morphology of the ZnO nanostructure was examined by field- emission scanning electron microscope (FESEM, JSM- 7600F). For pH sensing capability, the sensitivity measurement was taken using EGFET setup equipment as shown in Fig.1. ZnO nanostructure as the pH sensitive membrane and reference electrode was connected to a commercial metal- oxide semiconductor FET (MOSFET), which is connected to a readout interface circuit (ROIC). The sensitivity of ZnO thin film towards the pH buffer solution was measured by dipping the sensing membrane in pH buffer solution ranging from 4 to 12. The sensitivity values were obtained from the slope of the plotted graph $V_G$ versus pH level. Detailed measurement setup is described elsewhere [30].
3. Results and discussions

3.1. ZnO Growth Morphology

Fig. 2 FESEM images of ZnO nanostructures deposited at b) 200 c) 300 d) 400 e) 500 and f) 600 °C post annealing treatment. a) shows the as-deposited sample.
The surface morphology of ZnO nanstructures for as-deposited sample and annealed samples at various annealing temperatures are shown in Fig.2. From the figure, it can be seen that the as-deposited sample (Fig.2 (a) is ZnO nanorods. After the post-deposition annealing treatment at 200 to 600 °C, the ZnO nanorods agglomerated and formed the ZnO nanoflowers. Increasing the post annealing temperature caused the ZnO nanoflowers diameter and length to increase. Annealing process are known to improve the crystallinity of a material and at the same time may influence the growth direction. The increase in the annealing temperature means that higher energy received by the atoms to rearrange themselves [31] thus resulting in longer rod-petals.

3.2. pH Sensing Behaviour

| Table 1. The value of sensitivity and linearity for each sample annealed at various temperature |
|-----------------------------------------------|
| Sensitivity (mV/pH) | Linearity |
|----------------------|-----------|
| As-deposited          | 3.4       | 0.0683 |
| 200 °C               | 29.2      | 0.8476 |
| 300 °C               | 39.8      | 0.9672 |
| 400 °C               | 25.0      | 0.9658 |
| 500 °C               | 12.1      | 0.652  |
| 600 °C               | 19.0      | 0.8434 |

The sensitivity and linearity of the as deposited sample and annealed samples at various annealing time are shown in Table 1. The as-deposited ZnO nanostructure sample shows the lowest sensitivity and linearity as pH sensing membrane. The post annealing at 300 °C cause the improvement of sensitivity and linearity from 3.4 mV/pH, 0.0683 to 39.8 mV/pH, 0.9672. The lowest sensitivity of as-deposited sample may due to the low adhesion of ZnO nanorods with ITO substrate. The fabricated as-deposited samples were powder-like structures that make it easy to peel-off when immersed in pH buffer solutions. The improvement of the sensor performance may be due to the improvement of the crystalline quality. However, further improvement of the crystalline quality by the higher annealing temperature reduce the sensitivity and linearity of sample due to the reduction of binding sites in the membrane [32]. Binding sites are needed to react with H+ ions. According to the site binding theory, the number of binding sites residing on the sensing membrane could lead to changes in the surface potential voltage between the sensing layer and the electrolyte interface. The actual change of the surface potential voltage would depend on the pH value of the electrolytic solution. Based on the above-mentioned site binding model, the surface potential voltage (\( \psi_0 \)) between the sensing layer and the electrolytic interface can be expressed as [4]:

\[
2.303 \left( \text{pH}_{\text{pzc}} - \text{pH} \right) = \frac{q\psi_0}{kT} + \sinh^{-1}\left(\frac{q\psi_0}{kT} - \frac{1}{\beta}\right)
\]

where \( \text{pH}_{\text{pzc}} \) is the pH value at the point of zero charge, \( q \) is the electron charge, \( k \) is the Boltzmann's constant, \( T \) is the absolute temperature, and \( \beta \) is the sensitivity parameter. The relation between \( \beta \) and the surface sites per unit area (NS) can be expressed as
\[ \beta = \frac{2q^2N_s(K_aK_b)^{1/2}}{KTC_{DL}} \]  

(2)

where \( K_a \) and \( K_b \) are acid equilibrium constant and basic equilibrium constant, respectively, and \( C_{DL} \) is the capacitance of the electrical double layer derived by the Gouy-Chapman-Stern model. From the equation (1) and (2) it is clear that the sensitivity and the binding sites at the sensing membrane surface have obvious linear response, hence, this result can be attributed to a reduction in the hydride ion reaction site density (\( N_s \)) by the raised temperature.

4. Conclusions

The ZnO nanostructures was successfully deposited on ITO substrate using simple CBD process in water bath at 95 °C for 4 h. The post-deposition heat treatment on ZnO nanostructures samples was varied from 200 to 600 °C in order to study the effect of annealing temperature on ZnO nanostructures as sensing membrane. From the FESEM images, the as-deposited sample was nanorods structure. Applying the post heat treatment caused the ZnO nanorods to agglomerate on each other and formed the ZnO nanoflowers. The diameter of ZnO nanoflowers increased with the increased of annealing temperature. The XRD results showed that the intensity of ZnO (100) was increased when temperature was increased up to 500 °C before started to decrease at 600 °C. The as-deposited sample sensitivity is only 3.9 mV/pH with linearity of 0.0683. The sensitivity and linearity of the samples increased when the post heat treatment was applied. The highest sensitivity and linearity was obtained from the sample annealed at 300 °C, with 39.9 mV/pH sensitivity and 0.9792 linearity. The post annealed treatment improved the crystallite size which provided high surface area for sensing activity. From the site bonding model also, it can be concluded that the high temperature may induce the number of binding sites residing to reduce and thus the performance of ZnO nanostructures as EGFET sensing membrane decreased.

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