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Research paper

Thermal Chemically Deposited Zno Nanostructures: Influence of Post-Deposition Annealing Temperature on Ph Sensor Performance

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Abstract

Zinc oxide (ZnO) nanostructures were synthesized via thermal chemical deposition (TCVD) method and applied as the sensing membrane of an extended-gate field effect transistor (EGFET) pH sensor. The ZnO nanostructures undergone a post-deposition heat treatment with the temperature ranging from 200-500 °C for 15 min in air ambient. The influence of the post-deposition heat treatment on the physical and pH sensing characteristics was investigated. The FESEM images showed that the surface morphology of the samples were dependent on post-annealing treatment. The as-deposited sample showed the biggest grain size and non-uniformed structures. Applying the post-annealing heat treatment caused the surface morphology to become denser and uniform. The most ideal temperature for the heat treatment for EGFET pH sensor application was found at 300 °C resulting in a pH sensitivity of 48.2 mV/pH with 0.9646 linearity.

Keywords: *ZnO ;TCVD ; Annealing Temperature ; EGFET ; pH Sensor*

1. Introduction

pH level is fundamentally important in various biological and chemical reactions. Thus, pH sensors are considered as an important measurement in wide applications such as agriculture, food industries, medical field and so on. The pH sensors provide a logarithmic measurement of hydrogen ions that determined the pH level (Yoon et al., 2017). Conventionally, the level of pH was determined using paper strip or glass electrode. However, the paper strip can give only approximation instead of exact numerical value of pH level. Even though the glass electrode gives numerical value, but the glass electrode is expensive and have poor performance on low ionic strength solution (Pathak & Singh, 2017). In 1983, Van der Spiegel introduced extended-gate field effect transistor (EGFET) in order to overcome the drawbacks of conventional pH sensors. EGFET offers several advantages such as light and temperature insensitive, simple packaging and flexible (Das et al., 2014; Sabah, Ahmed, Hassan, & Almessiere, 2017a). The EGFET consists of metal oxide semiconductor field effect transistor (MOSFET) and a sensing membrane that is fabricated separately from FET in order to insulate the FET from measurement solutions. (Sabah, Ahmed, Hassan, & Almessiere, 2017b). The studies on nanostructures of metal oxide sensing membrane were done extensively because of its advantages in increasing the performance of pH sensors. The metal oxide semiconductors nanostructures were believed to possess high surface to volume ratio that lead to a short diffusion between measurement solution and sensing membrane surface (Cisternas, Ballesteros, Valenzuela, Kahlert, & Scholz, 2017; Yoon et al., 2017). Among metal oxide semiconductor materials, zinc oxide (ZnO) nanostructures had attracted much interest due to their excellence in terms of its mechanical, chemical and thermal stabilities. Besides that, ZnO also can be tuned into various morphology and contributes to high surface area for better sensing performance (Li et al., 2018; Narasimman, Balakrishnan, Meher, Sivacoumar, & Alex, 2017). The ability to fabricate, control and optimize the desired uniform morphology of nanosized ZnO with desired properties has generated a lot of interest due to fact that the sensing performance rely strongly on the particles morphology, and surface defect states. Therefore, controlling the surface defects has been validated as one of the effective approaches to improve the sensing properties. The findings indicate that, manipulation of surface defects can be easily achieved during material processing and annealing treatment (Muchuweni, Sathiaraj, & Nyakotyo, 2017; Shingange et al., 2017; Wang et al.).

There are several kind of method that were used to deposit ZnO nanostructures such as hydrothermal, dip-coating, immersion and also chemical vapor deposition (CVD). The CVD method can be considered as preferred methods in order to fabricate the ZnO nanostructures due its advantages such as high yield and purity, low cost and ability to adjust the deposition conditions (Pasha, Poursalehi, Vesaghi, & Shafiekhani, 2010).

In this paper, the ZnO nanostructures were fabricated using thermal CVD (TCVD) method for EGFET pH sensor sensing membrane. The nanostructures characteristics and pH sensing behavior dependence on the post-deposition heat treatment were studied.

2. Methodology

Indium tin oxide (ITO) covered glass was used as the substrate since EGFET sensing membrane need a conductive layer in order to transmit the potential difference signal to the MOSFET. Prior to the synthesis process, the ITO substrates were cleaned using methanol, and deionized water for 10 min each step, in an ultrasonic bath. The ITO substrates were then dried using nitrogen gas. TCVD setup with double furnace was used for deposition process. The Zn powder was used as precursor and was heated at 750 °C. The substrate temperature was fixed at 600 °C. 69 sccm of argon gas was flown throughout the experiment, while the oxygen as oxidation gas was flown only for 30 min during deposition process. The samples were then annealed in air ambient at various temperatures ranging from 200 to 500 °C. The as-deposited sample was prepared for comparison.

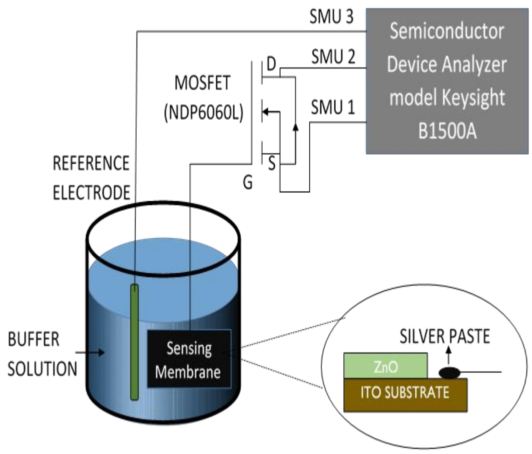

Fig. 1: EGFET pH sensing setup using semiconductor device analyzer (Keysight, B1500A)

The deposited samples were characterized for their structural and sensing properties. The field emission scanning electron microscope (FESEM) was used to examine the surface morphology of ZnO nanostructures while its ability as EGFET pH sensor sensing membrane was tested using Semiconductor Device Analyzer model Keysight B1500A as shown in Fig.1 above. The sensitivity and linearity of deposited samples was obtained from gradient and linear regression of Vref - pH graph, respectively.

3. Results and Discussion

3.1. Surface Morphologies of Zno Nanostructures

The surface morphology of ZnO nanostructures annealed at various temperatures are shown in Fig.2. For comparison, the surface of morphology for as-deposited sample is shown in Fig.2 (a). From the results, it can be seen that the grain size is largest and surface roughness is highest for as-deposited sample as can be seen in Fig.2 (a). Applying the post-deposition treatment causes the surface morphology of ZnO nanostructures to become denser and more uniform. This results indicates good crystal quality of the deposited films. The more uniform structure may reduce the boundaries energy between adjacent particles which aids the transport of electrons along the membrane surface without disruption (Sabah et al., 2017a). This result indicates that annealing process plays significant role in altering the surface morphology of ZnO nanostructures.

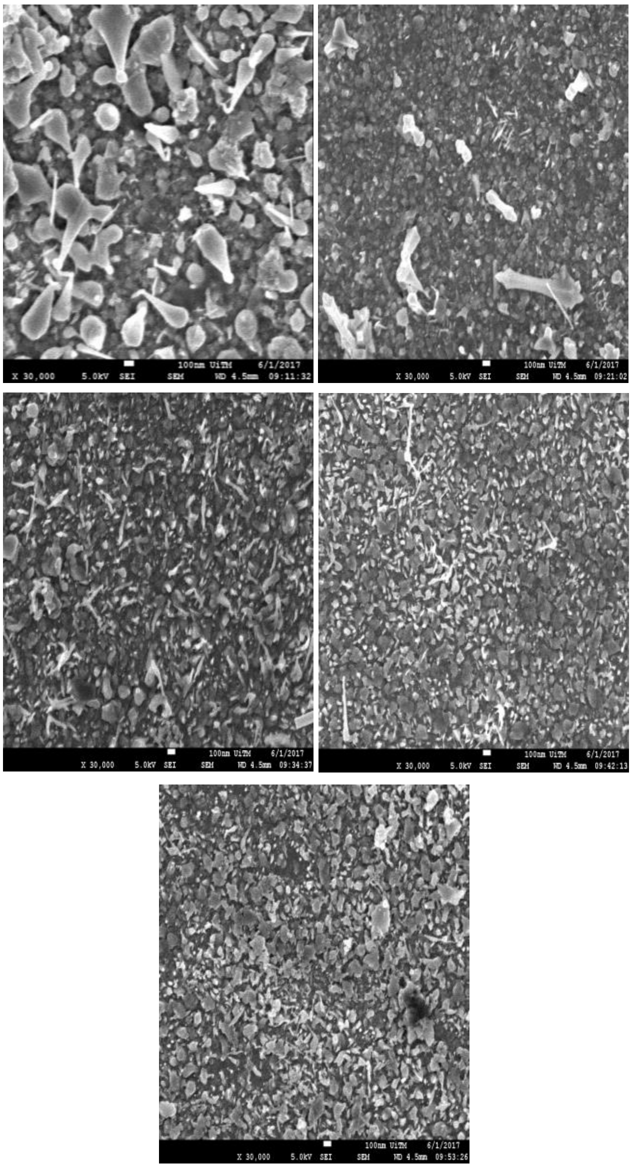

Fig. 2: FESEM images of ZnO nanostructures at b) 200, c) 300, c) 400 and d) 500 °C post-annealing temperature using TCVD while a) as-deposited sample

3.2. Ph. Characteristics

Fig.3 shows the transfer characteristics of the ZnO nanostructure samples in various buffer solutions of pH values between 4 to 12. Meanwhile, the corresponding sensitivity and linearity for each sample was tabulated in Table 1. This sensitivity was obtained from the gradient of Vref – pH graph plotted. Regression of the graph presents the linearity of the samples. In this experiment, the reference voltage (Vref) was swept from 1 to 2 V while the drain voltage (VD) was fixed at 500 mV. There are little different in behavior of the transfer characteristic where all the samples show that the threshold voltage was shifted from left to the right. In order to plot the Vref - pH graph, the value of Vref was taken from the transfer curve graph at ~100 µA ID for each of the pH value

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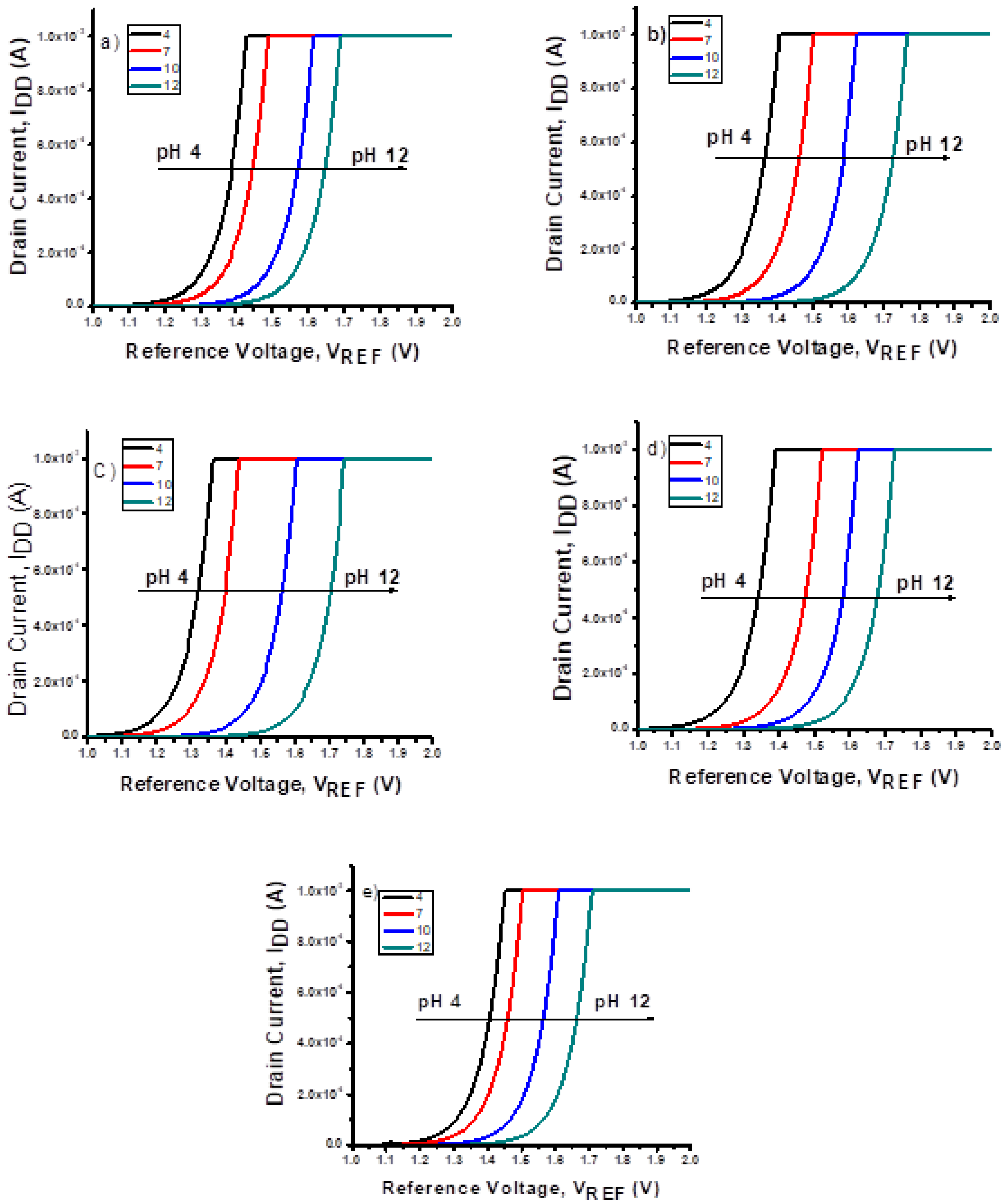

Fig. 3: Transfer curve characteristic for ZnO nanostructures at a) deposited-sample, b) 200, c) 300, d) 400 and d) 500 °C post-annealing treatment temperature

From Table 1, the sensitivity value for as deposited sample and samples annealed at 200, 300, 400 and 500 °C is 31.8, 44.0, 48.2, 41.0 and 32.3 mV/pH respectively. The best sensitivity of pH sensor was found when sample was being annealed at 300 °C. The performance of pH sensitivity is possibly related to the nanocrystallite size and also surface-to-volume ratio. Based on the FESEM results in Fig.2, the post annealing treatment caused the grain size to become uniform. According to F.A. Sabah et al, the uniform structures gives the high crystallite size and this may contribute to high surface to volume ratio of the sample and increase the number of sites that is needed for ion-exchange process in EGFET pH sensor mechanism (Sabah et al., 2017a).

Table 1: Sensitivity and Linearity value of the deposited samples obtained from Vref –pH graph (based on Vref taken at ~100 µA)

Post Annealing Temperature (°C)	pH Characteristic	
	Sensitivity (mV/pH)	Linearity
RT	31.8	0.9964
200	44.0	0.9721
300	48.2	0.9646
400	41.0	0.9965
500	32.3	0.9616

4. Conclusion

ZnO nanostructures were successfully deposited by TCVD method and applied as the as sensing membrane for EGFET pH sensor. From the FESEM images, it can be seen that the surface morphology for as-deposited sample was rough and has the largest grain size. Applying the post-deposition heat treatment improved the uniformity of ZnO nanostructures surfaces morphologies. The optimum post-deposition heat treatment was found at 300 °C that produced a sensing membrane with the sensitivity of 48.2 mV/pH with linearity of 0.9646. The highest sensitivity of EGFET pH sensor at 300 °C can be attributed to the improvement of the sample's surface morphology after the heat treatment process that increased the surface-to-volume ratio and lead to high site binding for ion-exchange process in pH sensor mechanism.

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