The growth of ZnO nanorods based on hydrothermal and measurement of conductivity

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Abstract. Zinc Oxide (ZnO) nanorods have been attracted interests as a gas molecule-catcher material in gas sensor applications. In this research, ZnO nanorods was grown on the surface of interdigitated electrode arrays substrate by using a hydrothermal method. The hydrothermal process consists of two steps, i.e., the seeding process and the growth of ZnO nanorods. The precursor material used in seeding process was Zinc Acetate Dihydrate (Zn(CH3COO)2.2H2O), while Zinc Nitrate Tetrahydrate (Zn(NO3)2.6H2O) was used as a precursor in the growth of ZnO nanorods. The sample was characterized by using scanning electron microscopy (SEM) and I-V Curve testing to determine the conductivity properties. SEM results show that ZnO nanorods has an average diameter of <100 nm. The result from the I-V curve with applied voltage in the range of 1–30 volt shows that the greater value of the applied voltage produces a decrease of the resistance value. The resistance value obtained at a given voltage of 1 volt is 7.8 kohm, while at a voltage of 30 volts is 0.5 kohm. The I-V curve profile indicates that interface between ZnO nanorods and Au-electrode shows a Schottky barrier characteristics. The gas effect with various parameters of CO gas concentrations, applied voltages and temperatures is under study.

1. Introduction

ZnO (zinc oxide) nanorods has attracted the interest of researchers to be developed, because it has high electron conductivity mobility and thermal stability [1], in addition ZnO belongs to a group of semiconductor oxide metals that have been studied for a long time and it is known that the metal oxide semiconductor material has advantages in good sensitivity to gas and the availability of abundant materials [2]. As an n-type semiconductor with wide energy band gap of 3.37 eV, ZnO has the exciton binding energy of 60 meV and can grow at low temperatures of below 500°C[3]. A lot of research have been done on the use of ZnO in various technologies, such as optoelectronic devices [4], solar cell [5], piezoelectric materials [6], and gas sensors [7-12]. In recent years growth of ZnO nanorods uses several methods including chemical vapor deposition [1], thermal evaporation [13], electrodeposition [14], vapor–liquid–solid (VLS) growth [6], and electrochemical deposition (ED) [6]. However, previous studies reported that the methods produced a quite large diameter of ZnO with a range of 100-700 nm and a length range of 1500-2000 nm.

Hydrothermal is a method that more efficient and economical to grow ZnO nanorods. Byrappa and Yoshimura defined hydrothermal as heterogeneous chemical reactions with the aqueous solvent above...
room temperature and at a pressure greater than 1 atm in a closed system [15]. Recently we have already studied about the growth of ZnO nanorods by hydrothermal method which generates an excellent morphology with the average diameter of 10 – 100 nm [15–23] and length of 100 – 2000 nm [2,9,10,17,19,20,25]. Additionally, researchers used the various substrate to grow ZnO nanorods, i.e. glass substrate [20] and Au-coated Alumina electrode [7]. However, the result showed that the diameter of ZnO rods on both substrates is 150 – 200 nm. The quite large diameter will decrease the number of contacts between the nanorods across the current path [7]. In this paper, we report the growth of ZnO nanorods using a hydrothermal method on an interdigitated electrode with the diameter size of less than 100 nm. A conductivity of ZnO nanorods on measured in order to investigate their electrical properties.

2. Methods
All chemicals are the commercial analytical class (Merck Co.Ltd). The precursor material used in seeding process was Zinc Acetate Dihydrate (Zn(CH$_3$COO)$_2$$\cdot$2H$_2$O), while Zinc Nitrate Tetrahydrate (Zn(NO$_3$)$_2$$\cdot$6H$_2$O) was used as a precursor in the growth of ZnO nanorods. Interdigitated electrodes with 150 nm Au layer and 10 µm interdigital gap from NanoSPR were used as a substrate.

The first step is seeding process Zinc Acetate Dihydrate (Zn(CH$_3$COO)$_2$$\cdot$2H$_2$O) and Diethylamine (C$_2$H$_4$N) were dissolved in Ethylene Glycol Monomethyl (C$_4$H$_9$O$_2$) with the concentrations 0.3 M. Then the solution is given a heat treatment up to 60°C to yield a homogeneous and stable colloid solution, which served as a seed solution[6]. The substrate was dipped in the solution in 3 times for 5 minutes, then the substrate was dried at 100°C for 1 hour and followed by an annealing process at 350°C for 2 hours.

Zinc Nitrate Tetrahydrate (Zn(NO$_3$)$_2$$\cdot$6H$_2$O) and Hexamethylene-tetramine (C$_6$H$_{12}$N$_4$) were dissolved in demineralized water with concentration 0.05 M to synthesize ZnO solution. Then hydrothermal process was carried out at 95°C for 2 hours. The morphology of ZnO nanorods was analyzed using Scanning Electron Microscope (SEM) in vacuum condition. The SEM image was used to measure the diameter of ZnO nanorods using infinity analysis software which provides advanced imaging for science, research and industry. Energy Dispersive Spectroscopy (EDS) analysis was used to observed the composition contained on the sample. Current – voltage characteristic (I – V curves) of ZnO were measured in order to investigate the electrical conductivity property.

3. Result and Discussion

3.1. Morphology and size distribution of the ZnO nanorods
The morphology of ZnO nanorods which was observed by Scanning Electron Microscope (SEM) is shown in figure 1. Figure 1 shows that ZnO nanorods can already be grown on the substrate using hydrothermal. SEM results in Figure 1 (a) show the growth of ZnO nanorods located in Aurum and SiO$_2$. From figures 1(b) and 1(c), it is known that the growth of nanorods on the substrate is homogeneous and the direction of growth tends to be perpendicular to the substrate, while in figure 1(d), a morphology of ZnO nanorods has Markowitz floral pattern. The diameter value of nanorods in sample was analyzed by infinity software using Figure 1 (b).

Figure 2 also indicates the various diameter of ZnO nanorods. Figure 2 shows a histogram of ZnO nanorods distribution on (a) Au pattern surface and (b) SiO$_2$ surface. On Au surface, it can be seen that the diameter of ZnO nanorods is in the range of 47-52 nm, while once on SiO$_2$ is in the range of 71 - 76 nm. This shows that ZnO nanorods are successfully grown on substrate in Au and SiO$_2$. 

### References

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Figure 1. Morphology of ZnO Nanorods on Interdigitated electrode at scale (a) 3µm, (b) 2µm, (c) 1µm and (d) 500 nm

3.2. Element composition
Figure 1(a) was analyzed using EDS to know the element composition. Element composition from the sample is shown in figure 3. The element is Si, Au, Zn, and O. A significant value of Zn identified that the growth of ZnO nanorods on the substrate were evenly distributed and there were no impurities in the sample. EDS results show that there are elements of O, Si, Zn and Au with values of 13.07 wt% (45.15 atomic%), 1.04 wt% (2.06 atomic%), 38.28 wt% (32.29 atomic%), and 46.06 wt% (12.93 atomic%), respectively. Based on EDS result it is known that the atomic percentage of Zn and O does not have much difference. The atomic percentage value in O is greater than Zn one because of the substrate containing the SiO₂ element.

3.3. Conductivity
Figure 4 shows that the increase in voltage results in decreases of the resistance value. When the voltage applied is 1 V, the resistance value becomes 7.8 kohm, while for a voltage of 30 V the resistance value is obtained at 0.5 kohm. The voltage applied at 1 V contact between the metal and semiconductor reaches thermal equilibrium conditions, where electrons flow from the semiconductor to the metal passing through the barrier causes a larger resistance value [26]. Based on the theory of Schottky barrier figure 5 indicate a forward bias incident with ohmic contact characteristics, because the current is proportional to the voltage. The data profile follows the theory of Schottky barrier where the current flow is dominated by the electron flow from Au metal to the ZnO semiconductor nanorods in forwarding bias conditions [26].
Figure 2. (a) Diameters of ZnO Nanorods on Au (b) Diameters of ZnO nanorods SiO₂

Figure 3. EDS investigation of ZnO Nanorods
Figure 4. The relationship between the voltage and the resistance of the sample

Figure 5. The relationship between Current and voltage

4. Conclusion
In this study, ZnO nanorods have been successfully synthesized by hydrothermal method using interdigitated electrode as the substrate. SEM and EDS were used to know the morphology and composition on the sample, and conductivity measurement to know the conductivity. SEM analysis shows that the diameter of ZnO nanorods is less than 100 nm on Au surface which is smaller than on the SiO$_2$ surface. The diameter of ZnO nanorods on Au surface is in the range of 47-52 nm, while once on SiO$_2$ is in the range of 71 - 76 nm. This case indicates that the different elements of the substrate can affect the morphology of the resulting nanorods. Conductivity measurements also show the existence of Schottky barrier in the sample.

Reference
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