Micro structure of hydrothermal ZnO rods on micro cantilever surface

A S Budi1,*, M Y Frestika1, D Mulyati1 and R Nurjadi2

1Physics Department, Faculty of Mathematics and Natural Sciences, Universitas Negeri Jakarta, Indonesia
2Center for Materials Technology, Agency for the Assessment and Application of Technology, Puspiptek Building No. 224, Tangerang Selatan 15314, Banten, Indonesia

*Corresponding author: agusbb@unj.ac.id

Abstract. This study reports the microstructure of Hydrothermal ZnO rods on Micro cantilever Surface. Synthesis of ZnO rods consists of two processes e.g. a formation of seed layer using Zinc acetate dihydrate by a dip-coating and a growth of the ZnO rods using Zinc-Nitrate-Tetrahydrate at temperature 95°C for time variations of 1 hours, 2 hours, 3 hours, 4 hours, 5 hours, and 6 hours. Drying condition for both seed layer and growth of ZnO rods was done at a temperature of 120°C for 2 hours. The characterization of ZnO rods morphology was done by Field Emission-Scanning Electron Microscopy (FE-SEM), chemical element composition was performed with Energy Dispersive Spectrometry (EDS), crystal structure was done by X-ray Diffraction (XRD) and functional group analysis was done by Fourier Transform Infrared (FTIR). The characterization results show that the formation of Zinc Oxide with confirmed hexagonal form of FE-SEM and XRD results. The FE-SEM results show that the variation in growth time has an effect on the diameter size formed above the microcantilever. The longer the growth time, the larger the diameter of ZnO rods.

1. Introduction

Microcantilever has great potential for sensor applications in the medical, chemical and environmental fields because it has high sensitivity [1-4]. For this sensor application, microcantilever in the design is very flexible so it will be easy to bend if there is a virus object (molecules or particles) attached on the microcantilever surface. The microcantilever sensor measures the size of the microcantilever deflection because of the object. With such a mechanism, microcantilever sensors can detect biological and chemical objects that have mass in the femtogram order (10^{-15} grams) [2-4]. Some records can also detect up to attograms (10^{-18} grams) order, a record detector rarely used by other types of sensors [5-7]. During this time, various studies related to microcantilever sensors both theory and experiments have been done to explore the potential and to improve the performance. In addition to the sensitivity problem, selectivity is an important parameter in the sensor.

Although research on ZnO synthesis has been carried out by some research groups [8-9], but the growth of ZnO above the microcantilever for sensor applications is rarely performed [10]. In this research we will examine the effect of time variation of ZnO rods which is processed in 1-6 hours, apply on the morphology, chemical element composition, crystal structure and metal bond formed on
microcantilever surface by using hydrothermal method. The analysis parameters used include XRD, FE-SEM, EDS and FTIR.

2. Methods
The growth process of ZnO rods in this study is using hydrothermal method consisting of two processes called seed layer coating and the process of growing ZnO rods. For more details, the growth process is described as below.

2.1. The process of coating seeds (seed layer) on the microcantilever surface
The materials used in the process of seed coating on the surface of microcantilever is Diethylamine (C₄H₁₁N), Etylene Glycol Monomethyl (C₄H₁₀O₂), and Zinc Acetate Dihydrate (Zn (O₂CH₃)₂(H₂O)₂) with a concentration of 0.3 M. Microcantilever which has a small size (micrometer) causes the synthesis process is not easy to do (Figure 1). Therefore, a clamp holder is made to facilitate the dip-coating process. The clamp holder is made with some materials such as acrylic, magnet, aluminum and iron-based bolts. In Figure 2 we can see the design of the clip holder that has been created. Acrylic is perforated then magnets are embedded in it to attract aluminum to be used as a microcantilever clamp. In Figure 2, a pre-made dip-coating (holder) and microcantilever has been installed. The dip-coating process is carried out by dipping the holder together with the microcantilever into the solution then transferred to an empty beaker within 5 minutes each with repetition for three times. After the dip-coating process, dry with temperature of 120°C for 2 hours.

Figure 1. Clamp holder is used for dip-coating process

Figure 2. The dip coating process of microcantilever
2.2. The growth of ZnO rods on the surface of the microcantilever

The materials used in the growth process of ZnO rods on the surface of the microcantilever are Zinc Nitrate Tetrahydrate (Zn(NO$_3$)$_2$6H$_2$O), Hexamethylene-tetramine (C$_6$H$_{12}$N$_4$) and Aqua Deminerality (Aqua Dm) with concentration of 0.05 M. The growth of ZnO on the surface of microcantilever is using hydrothermal method. The coated microcantilever is dipped into the solution with the ingredients mentioned before for the growth process. The growth process of ZnO uses an oven with a temperature of 95°C for the time varied in 2 hours, 4 hours and 6 hours. Note that after ZnO growth process there should be an annealing process with temperature 300°C, this has to be done according to ZnO growth reference of the previous research [7], but in this research, we only done the drying process with temperature 120°C for 1 hour because the holder used which is made of acrylic, has the melting point of 160°C. Therefore, this process use oven instead of furnace. In the ZnO growth process with a temperature of 95°C, the solution precipitate and then it is dried at a temperature of 120°C until the precipitate forms a powder that will be used in the characterization process.

3. Results and Discussion

Figure 3 shows a microcantilever image scheme and FE-SEM characterization test results from a sample with a 2-hour growth time at 50000x magnification. The shape of the rods is the ZnO rods. Here, the directions of the growth of all ZnO rods are not exactly pointing upward. Some of the growth of ZnO rods goes upward, some others are with a certain angle, or even sideways direction (horizontal). Table 1 shows the distribution of ZnO rods diameter in the FE-SEM image. It can be seen from Table 1 that the growth diameter distribution of ZnO rods for variations in time of 2 hours has interval of 40-179 nm. The diameter indicating the largest frequency is the size of 120-139 nm.

![Microcantilever scheme and image characterization test results FE-SEM in 2 hours growth time](image)

**Figure 3.** Microcantilever scheme and image characterization test results FE-SEM in 2 hours growth time

| The size diameter interval (nm) | Frequency (piece) |
|-------------------------------|-------------------|
| 40-59                         | 5                 |
| 60-79                         | 4                 |
| 80-99                         | 17                |
| 100-119                       | 8                 |
| 120-139                       | 34                |
| 140-159                       | 4                 |
| 160-179                       | 2                 |

Table 1. The size diameter interval of FESEM ZnO rods in the growth time of 2 hours

Figure 4 shows the FTIR spectrum of Zinc Nitrate Tetrahydrate (Zn(NO$_3$)$_2$6H$_2$O), as well as FTIR spectrum of ZnO rods precipitation with the time of 2 hours, 4 hours and 6 hours. Wavelength 540 cm$^{-1}$ shows the formation of Zn-O bonding for 2 hours of growth time, while the wavelength of 548 cm$^{-1}$ and 547 cm$^{-1}$ show the growth of ZnO rods in 4 hours and 6 hours respectively. It is known from previous work that the wavenumber spectrum of ZnO nanoparticle growth is 532 cm$^{-1}$ [11].
Figure 4. Spectrum of zinc nitrate tetrahydrate (Zn(NO$_3$)$_2$6H$_2$O) and ZnO solution precipitation used for growth in 2 hours, 4 hours and 6 hours

Table 2. The crests and troughs appear on the base material of zinc nitrate tetrahydrate

| IR Absorption (cm$^{-1}$) | Bonding that cause absorption |
|--------------------------|------------------------------|
| 3337.20                  | O-H                          |
| 1637.35                  | C=O                          |
| 1537.22                  | NO$_3$                       |

Table 3. The crests and troughs appear of ZnO precipitation growth in the time of 2 hours

| Absorption IR (cm$^{-1}$) | Bonding that cause absorption |
|---------------------------|------------------------------|
| 3347.18                   | O-H                          |
| 1368.78                   | C-H                          |
| 881.69                    | O-H                          |
| 540.96                    | M-O (Zn-O)                   |

Table 4. The crests and troughs appear for a 4-hour ZnO precipitation growth time

| Absorption IR (cm$^{-1}$) | Bonding that cause absorption |
|---------------------------|------------------------------|
| 3455.96                   | O-H                          |
| 1356.20                   | C-H                          |
| 825.69                    | C-H                          |
| 548.27                    | M-O (Zn-O)                   |

Table 5. The crests and troughs appear for a 6-hour ZnO precipitation growth time

| Absorption IR (cm$^{-1}$) | Bonding that cause absorption |
|---------------------------|------------------------------|
| 3369.97                   | O-H                          |
| 1355.73                   | C-H                          |
| 820.58                    | C-H                          |
| 547.27                    | M-O (Zn-O)                   |
Table 2-5 show several bonds that cause the absorption on the base material Zinc Nitrate Tetrahydrate which is O-H, C=C, NO₂. While the bonds that cause absorption at 2 hours, 4 hours and 6 hours of growth precipitation are O-H, C-H and Metal Oxide (M-O) predicted as Zinc Oxide (ZnO). The O-H bonds absorbed in the spectrum region of the wave number around 3300 cm⁻¹ decrease when the ZnO rods grows in the longer time. It also occurs in C-H and O-H bonds in other spectrum areas. While the C=C bonds, there is no longer absorption in the NO₂ precipitation with a growth time of 2 hours, 4 hours and 6 hours. The metal oxide bond (M-O) predicted as a Zn-O bond is present in the spectrum of the wave number 540-548 cm⁻¹. Therefore, FTIR characterization analysis confirms the Zn-O bond in ZnO growth in this study.

4. Conclusion
ZnO material has been done on micro cantilever surfaces and investigations using FTIR. The functional groups of the FTIR testing were performed using ZnO rods zinc powder. The FTIR characterization test results that some spectrum of wave numbers emerge as a response of the bonds between particular atoms. The metal oxide bond formed from the base of ZnO rods is Zinc Nitrate Tetrahydrate (Zn(NO₃)₂6H₂O). With the longer growth time of 2 hours, 4 hours and 6 hours, the O-H and C-H bonds decrease the absorption rate. The formation of Zn-O atomic bonds for all three samples of ZnO rods (growth time of 2 hours, 4 hours and 6 hours) is indicated by the spectrum of the wave number around 540-548 cm⁻¹. Acknowledgments

References
[1] Fróméta N R 2006 Biotecnología Aplicada 23
[2] Raiteri R, Grattarola M, Butt H, and Skládal P 2001 Sens Actuators B 79115
[3] Vashist, S K 2007 J Nanotechnol 3 1
[4] Dohn S, Sandberg W, and Boisen A 2005 Appl Phys Lett 86 233
[5] Ratno N and Lia A 2013 Prosiding InSinAs 2012
[6] Contineau T, Sergey N, and Pronkin 2013 Sens Actuators: B Chem 182 489
[7] Killinc N and Cakmak O 2014 Sens Actuators B: Chem 202 357
[8] Singh N 2012 J Light Electron Optics 123 1340
[9] Kumar S 2014 Synthesis of ZnO Nanorods using Hydrothermal Method for natural Dye Sensitized Photovoltaic Cell
[10] Pavia D L, Lampman G H, and Kriz G S 2001 Introduction to Spectroscopy 3th ed (USA: Thomson Learning)
[11] Bagheri S 2013 Der Pharma Chemica 5 265