The Growth of ZnO Nanorods on Stainless-steel foils and Its Application for Piezoelectric Nanogenerator

Nandang Mufti1,3,*, Anggreta Damayanti1, Aripriharta2, Arramel4, Ahmad Taufiq1,3, Sunaryono1,3

1Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia
2Department of Electrical Engineering, Faculty of Engineering, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia
3Centre of Advanced Materials for Renewable Energy, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, Indonesia
4Department of Physics, National University of Singapore, 2 Science Drive 3, 117542, Singapore

*Corresponding author’s email: nandang.mufti.fmipa@um.ac.id

Abstract. ZnO nanorods have attracted much attention because of their potential for harvesting energy device. In this study, we investigate the effect of hexamethylenamin concentration to a characteristic of ZnO nanorods on stainless-steel foil. ZnO nanorods were synthesized by simple hydrothermal methods on Stainless-steel (SS) by varying the precursor ratio of hexamethylenediamine and Zinc nitrate tetrahydrate. The ZnO nanorods samples were characterized by X-ray diffraction for crystal structure properties, and Scanning Electron Microscope (SEM) for their morphology. The piezoelectric nanogenerator performance was characterized by measuring current and voltage with electrometer and oscilloscope, respectively. The lattice parameters of ZnO nanorods are a, b = 3.2495 Å, and c = 5.2069 Å with the ratio c/a is 1.6 indicating that ZnO nanorods have hexagonal wurtzite structure. The length and of ZnO nanorods increases by increasing the precursor ratio from 0.347 to 1.229 µm. However, the diameter can be varied from 63 to 102 nm. The small diameter and longest of ZnO nanorod are the best for nanogenerator applications.

Keywords: Growth, ZnO Nanorod, stainless-steel, piezoelectric, nanogenerator

1. Introduction
The desire to produce self-powered electronic led to increasing the research in energy harvesting device in the last few years [1]. Along with the progress in nanotechnology, the demand for low power consumption in electronic applications has attracted much attention. One way to solve this problem is by using an energy harvesting device that can collect energy from environmental vibration by using piezoelectric materials [2,3]. Piezoelectric materials have a unique ability to convert mechanical vibrations into electrical energy, and this material becomes a very promising for the renewable energy source. Many studies have been interested in the use of one-dimensional (1D) piezoelectric nanostructures such as PZT, BaTiO3, CdS, ZnO, and TiO2 for mechanical energy harvesting [4]. ZnO is one of an n-type semiconductor that has a wide band gap of 3.37 eV with an excitonic binding energy
of about 60 meV at room temperature [5]. Moreover, ZnO is also relatively cheap material, non-toxic, environmentally friendly and has been widely used in applications such as light-emitting diodes [6], UV sensors [7], Gas Sensors [8], and Solar Cells [9]. ZnO in the form of nanorods can improve physical properties such as light absorption, due to its high surface area [10].

ZnO nanorods (ZnO NRs) have high piezoelectric coefficient values and can be grown at low temperatures on almost any kind of substrate. Piezoelectric properties of ZnO can be utilized to convert the environmental vibration into electricity called piezoelectric nanogenerators. However, the current and voltage generated by ZnO nanorods are still relatively small and grown on the ITO/FTO substrate. In order to improve the efficiency of nanogenerator, it important to optimize the ZnO NRs growth to increase the total surface area by tuning growth parameters such as the concentration of precursor, growth temperature, time, [11]. Therefore, we investigate the effect of precursor concentration between zinc nitrate tetrahydrate (ZNT) and Hexamethylenetetramine (HMT) to characteristics of ZnO NRs on stainless-steel foil due to cheaper and good conductivity.

2. Materials and Methods

The ZnO NRs were grown by the hydrothermal method on a stainless-steel foil. The stainless-steel foil was cleaned by dipping into acetone on the ultrasonic cleaner for 10 minutes, then washed with deionized water. Then, the stainless-steel is stored and dried on a clean tissue. ZnO solution was made by dissolving the Zn-acetate powder (Zn(CH\textsubscript{3}COO)\textsubscript{2} \cdot 2H\textsubscript{2}O) in ethanol solution. The mixture was heated and stirred at temperature of 70 °C for 45 minutes by magnetic stirrer hotplate. Then, Monoethanolamine (MEA) was added dropwise to the solution at temperature of 700 °C for 2 hours. The concentration ratio between Zn-acetate and MEA is equal. The solution was cooled at room temperature for 24 hours.

ZnO films were synthesized by a spin coating method. The ZnO solution was dropped on the clean stainless-steel substrate that was placed on the spin coater plate, then spinning at 300 rpm for 25 seconds. The preheating substrate was done at 150 °C for 10 minutes, whereas the annealing of ZnO film was done at 550 °C for 2 hours.

ZnO NRs were grown by the hydrothermal method. The growth solution was prepared using zinc nitrate tetrahydrate (ZNT) and Hexamethylenetetramine (HMT) in deionized water. The concentration of zinc nitrate tetrahydrate was 45 mM, and the concentration of HMT was varied at 45 mM, 56 mM, and 68 mM. Therefore, the molar ratio between ZNT and HMT was 1: 1.1; 1.25; and 1: 1.5. The solution was stirred using a magnetic stirrer for 45 minutes at room temperature. Then, the ZnO film was immersed in the prepared solution for 6 hours with temperature of 90 °C. The sample was washed with DI-Water to remove the salt residue from the sample surface and was dried with a dry blower. Finally, The ZnO NRs on the Stainless-steel foil were annealed at 550 °C for 2 hours in the furnace. Beside ZnO nanorods, The PVA films on stainless-steel foil was prepared by using spin coating method with speed of 3000 rpm for 20 seconds.

All ZnO nanorods samples were characterized by X-ray diffraction (XRD) for structural properties investigation. Scanning Electron Microscope (SEM) to determine the length and the diameter of ZnO nanorods. The oscilloscope was used for voltage measurements.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of ZnO NRs with variations of precursors ratio between ZNT and HMT. The XRD patterns of ZnO seed layers and ZnO NRs are similar to high-intensity peak at the Bragg plane of (100), (002), and (101). Other peaks are also observed as stainless-steel peaks. The crystal structure of the ZnO NRs was analyzed using Rietica software and summarized in Table 1. The lattice parameters of ZnO NRs and ZnO bulk from JPCDS standard (No. 36-1451) were alike, that is \(a,b = 3.2495 \text{ Å}\), and \(c = 5.2069 \text{ Å}\) with the ratio \(c/a\) is 1.6 indicating that ZnO nanorods have hexagonal wurtzite structure. This result is similar with lattice parameters of ZnO NRs that previously reported [12,13].
Figure 1. The XRD patterns of ZnO nanorods with different precursor concentration ratio between ZNT and HMT

The lattice parameter indicated that the ZnO NRs had a crystalline form and a single phase. The peak (101) was seen to have a higher intensity compared with other peaks, except for the ZnO NRs with precursor concentration ratio of 1:1.25 that has the highest peak (002). It indicated that the ZnO NRs grew along the $-c$ direction, while the peak (101) was caused by the growth of some nanorods that was out from the c-direction. The growth orientation of ZnO NRs on the plane (002) was similar to results that reported by other researchers [9,14].

| Lattice Parameters | Model ZnO | ZnO NRs 1:1 | ZnO NRs 1:1.25 | ZnO NRs 1:1.5 |
|--------------------|-----------|-------------|----------------|--------------|
| $a = b$(A)         | 3.249     | 3.2495      | 3.2495         | 3.2495       |
| $c$(A)             | 5.2038    | 5.2069      | 5.2069         | 5.2069       |
| $c/a$              | 1.6       | 1.6         | 1.6            | 1.6          |

Figure 2 shows SEM photos of ZnO NRs at different precursor concentration ratio between ZNT and HMT. The morphology of ZnO nanorods leads to a hexagonal form. The highest diameter shows at ZnO nanorods with precursor concentration ratio of 1:1.25 that has the highest peak (002). In general, the thickness of ZnO NRs increases by increasing precursor concentration. The longest rod obtained at precursor concentration ratio 1:1.5. The diameters and rod lengths summarized in Table 2. However, the diameter of ZnO NRs varies between 63.4 to 102.5 nm.

| precursor concentration ratio between ZNT and HMT | Length of ZnO nanorods (µm) | Diameter (nm) |
|-----------------------------------------------|-----------------------------|---------------|
| 1:1                                           | 0.347                       | 63.4          |
| 1:1.25                                        | 0.437                       | 102.5         |
| 1:1.5                                         | 1.229                       | 73.4          |
In order to measure the nanogenerator performance of ZnO NRs, the voltage of ZnO NRs that have been combined with PVA measured by oscilloscope as shown in Figure 3. The results show that ZnO nanorods at precursor concentration ratio between ZNT and HMT at 1:1 and 1:1.5 has the highest voltage of around 2.6 Volt. This output Voltage is higher compared with nanogenerator from ZnO/PVA nanofiber previously reported [15]. However, the voltage fluctuations at 1:1.5 is more stable rather than 1:1. The voltage measurement was done by pressing ZnO NRs/PVA around 6 N/m². This result indicates that small diameter and longest of ZnO NRs are the best for nanogenerator applications due to the large surface area.

4. Conclusion
The ZnO nanorods on Stainless-steel foil have been successfully synthesized by simple hydrothermal methods. The crystal structure of ZnO nanorods is hexagonal wurtzite with a, b parameters of 3.2495 Å, c-parameter of 5.2069 Å and c/a ratio of 1.6. The increasing precursor concentration ratio between ZNT and HMT increases the length of ZnO nanorods from 0.347 µm for 1:1, to 0.437 µm for 1:1.25 and 1.229 µm for 1:1.5. While the diameters of ZnO nanorods are varying between 63.44 nm to 102.5 nm. The best and stable output voltage of 2.6 volt obtained at precursor concentration ratio 1:1.5 indicating that small diameter and longest of ZnO nanorod is the best for nanogenerator applications.

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