Nickel Doping in ZnO Nanorod Synthesis: Effects of Nickel Concentration on Physical Properties of the Nanorod

Iwantono*, Catherine Hutagaol*, Truly Theresia Saputrina, Awitdrus

Department of Physics– FMIPA, Universitas Riau
Jl. HR Soebrantas, Km. 12.5, Pekanbaru, 28293, Indonesia

*iwantono@lecturer.unri.ac.id, cthrnmnc@gmail.com

Abstract. ZnO nanorods have successfully been grown on the surface of FTO. The growth of ZnO nanorods was carried out using the seed-mediated growth method, whereas the Ni doping was carried at different concentrations. The effect of nickel doping on ZnO nanorods was observed using field emission scanning electron microscope (FESEM), UV-Vis spectroscopy, and X rays diffraction (XRD). ZnO nanorods having hexagonal shape were shown by FESEM images, and overlap of ZnOnanorods forming a nanoflowers with wider rod size. UV-Vis spectra showed that strong absorption occurred at a wavelength of 390-300 nm, the highest intensity of absorption was resulted by 15mM sample. The energy gap of the sample decreased as increasing its concentration. XRD pattern of the samples showed the diffraction peaks occurred at angles of $2\theta = 31.72^\circ$, $34.45^\circ$, $36.20^\circ$, $47.50^\circ$, and $56.57^\circ$ that represented the crystal plane orientation of (100), (002), (101), (102), and (110).

1. Introduction

Indonesia is the major exporter for nickel in recent years. The use of nickel in metal alloy production to the electric storage device. Nickel also considered a good dopant for semiconductor production. Nickel was a promising metal to improve active materials for solar cells, especially dye-sensitized solar cells (DSSCs) which quietly interesting to study. Metal doping can improve and control the physical properties of active materials, such as charge carrier, optical properties, and nanostructure size [1]. In solar power conversion, DSSCs are third-generation solar cells composed of several main components, namely the working electrodes, electrolytes, and opposing electrodes [2]. DSSC was fabricated with an efficiency of 11% in 2004 by Gratzel using TiO$_2$ as active material [3].

Zinc oxide (ZnO) is a semiconductor that has the potential to replace TiO$_2$ in DSSCs working electrodes because it has an advantage as an active material for solar cell applications, such as gap energy of 3.37 eV which close TiO$_2$ gap energy (3.2 eV) [4]. This band was a direct bandgap of the valence band the conduction band, thus allowing faster excitation of electrons during the absorption of photon energy from sunlight by DSSCs [5].

This study is aimed to reveal the contribution of nickel dopant to the physical properties of ZnOnanorods. Nickel (Ni) is one of the transition metals with atomic number 28. The nickel doping into the ZnO crystal lattice is expected to improve the physical properties of the ZnO thin film. The energy bandgap of Ni is 3.6-4.0 eV [6], so that Ni has functional properties that are suitable and promising to be used as dopants in doping ZnOnanomaterials.
2. Methods

2.1. Preparations and characterization tools
ZnO nanomaterials are synthesized by the seed-mediated hydrothermal method which is divided into two stages, namely the seeding stage and growth phase. The main chemical reagents in this study include hexamethylenetetramine (HMT), zinc acetate dehydrate (ZAD), zinc nitrate hexahydrate (ZNH), and nickel (II) nitrate hexahydrate. Characterization of the samples was carried out using a field emission scan electron microscope (FESEM), UV-Vis absorption spectroscopy, and X-ray diffraction (XRD).

2.2. ZnO nanorod synthesis
The seeding phase started by mixture a seeding solution using 0.01 M ZAD and ethanol. Then, a 50µL seeding solution is dispersed on the surface of the FTO substrate using a spin coater by two-speed stages. The first speed is tuned to 2000 rpm for 30 seconds and the second speed is 3000 rpm for 50 seconds. Then, the sample is heated on a hot plate at 100°C for 15 minutes and dried out until the temperature drops to 60°C. The seeding process was repeated three times then to remove the remaining organic matter from the sample. In the last step, the sample was annealed at 275°C for 1 hour.

The growth stage is carried out by mixing 0.02 M ZNH and HMT into 20mL DI water. Nickel (II) Nitrate (Ni(NO$_3$)$_2$) as a doping solution was added to the growth solution with a concentration of 15mM and 20mM. The substrate samples were arranged into a synthesis bottle and added to the mixture of the growing solution. Samples were placed in the oven at 90°C for 7 hours, rinsed, and annealed at 250°C for 30 minutes.

3. Results and Discussion
Photographs of the FESEM scan are shown in Figure 1 which shows the nanostructure formed in the form of a nanorod in a hexagonal cross-section. Figure 1.(a) shown that pure ZnOnanorods are vertical or upright to the FTO substrate and homogeneous nanorod size with high density. Figure 1.(b) and (c) show that the nanorod rearrange their orientations, merge, overlap, and resemble nanoflower forms. The presence of Ni doping also results in a larger size of the nanorod, which indicates that the Ni atom is substituted into the ZnO nanorod lattice [7].

![Figure 1](image_url)

Figure 1. Photograph of FESEM for morphological structure of ZnOnanorods: (a) pure, b, ZnO:Ni 15mM, and (c) ZnO:Ni 20mM.
Figure 2. Absorption of UV-Vis spectrum of each sample.

The UV-Vis absorption spectrum of the sample is shown in Figure 2. In Figure 2 the absorption is weak or even almost invisible absorption at a wavelength of 800-400 nm. Significant absorption increases occur at wavelengths of 400-300 nm, namely in the UV light spectrum which has greater energy compared to visible light in the wavelength range of 800-400 nm. The strong absorption that occurs at these wavelengths is in accordance with the characteristics of the UV-Vis absorption spectrum of the ZnO nanorod with a hexagonal cross-section showing strong absorption occurs at a wavelength range of 200-400 nm [8].

Figure 3. Plot $(\alpha h\nu)^2$ against $h\nu$ for direct bandgap estimation.

Bandgap energy of the samples was measured using a linear curve extrapolation technique $(\alpha h\nu)^2$ vs $h\nu$ of all samples (Figure 3). In Figure 3, it can be seen that the effect of adding Ni to the ZnO nanorod results in a smaller energy gap value. The decrease in ZnO bandgap is greater with the higher concentration of Ni, which is 3.30 eV, respectively; 3.21 eV and 3.16 eV for pure ZnO and ZnO with Ni dopant of 15 mM and 20 mM. The lower the gap energy value, the higher the absorption of the sample to the incident light [9].

The XRD pattern of ZnO pure and ZnO Ni-doped samples are shown in Figure 4. In this figure it can be seen that all samples show diffraction peaks at an angle of $2\theta = 31.72^\circ$; 34.35$^\circ$; 36.20$^\circ$; 47.50$^\circ$ and 56.57$^\circ$. Evaluation using Eva Diffract Plus® confirms the five diffraction peaks are representations of the orientation of the crystal plane namely (100), (002), (101), (102), and (110)
which identify the ZnO peak which is the orientation of polycrystals with hexagonal structure [10]. The evaluation results also state that the strongest line of the peak diffraction sample is the peak (101).

![XRD pattern for all samples.](image)

**Figure 4.** XRD pattern for all samples.

![Diffraction peaks of crystal orientation of (101).](image)

**Figure 5.** Diffraction peaks of crystal orientation of (101).

Figure 5 shows the strongest peak shift with the presence of Ni in the ZnOnanorod. The diffraction peak shift indicates that there is a change in the crystal structure or changes in the crystal lattice parameters [11, 12]. The shifting of the peak (101) is caused by differences in the diameter of the Ni and ZnO ions, namely 0.138 nm (Ni) and 0.148 nm (ZnO). This difference in diameter causes the highest diffraction peak of the sample to shift towards a greater diffraction angle (right).

4. Conclusion

ZnO nanomaterials doped Ni have been successfully grown on the FTO substrate using seed-mediated hydrothermal methods with a concentration of Ni-doped 15 mM and 20 mM. The photos of the FESEM sample show that nanomaterials that grow in the form of nanorods are altered by Ni doping, which is the arrangement of the nanorods to overlap so that it resembles a nanoflower. The UV-Vis spectrum of the sample shows that strong absorption occurs in the range of the UV light spectrum, that is, at a wavelength of 300-400 nm. The XRD pattern of the sample shows that 5 diffraction peaks occur at an angle of 2θ = 31.72°; 34.35°; 36.20°; 47.50° and 56.57° with the orientation of the crystal plane (100), (002), (101), (102) and (110) with the highest diffraction peak or strongest line being in
the orientation of the Crystal plane (101) which experienced a slight shift to the right with the Ni doping.

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