The enhanced of photoresponse of ZnO nanorods film-coated by Cu$_2$O

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Abstract. Light detectors are widely used in generating energy from sunlight, medicine, space communications, ozone layer monitoring and missile warning systems, and others. The active materials that potential used as a detector of visible light and UV is ZnO. However, ZnO has a high bandgap of 3.04 eV so it is not suitable for absorbing light at short wavelengths. Cuprous oxide (Cu$_2$O) is a p-type of semiconductor with a small band, therefore it can increase the wavelength absorption range. The aim of this study is to improve the light response of ZnO nanorods by coating Cu$_2$O. The samples were characterized by X-ray Diffractometer (XRD), Scanning Electron Microscopy (SEM), UV-Vis Spectrometry, FTIR, and photoresponse test. The results show coating Cu$_2$O on ZnO nanorods succeeded in reducing the bandgap value, which is 2.47 eV. Reducing the band gap value is in accordance with the photoresponse test. The response of a sample that has a small bandgap is a fast response.

Keywords: Photoresponse, ZnO Nanorods, Cu$_2$O

1. Introduction
Photodetectors (PDs) have received more attention due to various potential applications in medicine, space communications, ozone layer monitoring, and missile warning systems, etc. [1]. Many semiconductor materials are used for fabricating photodetectors such as GaN, TiO$_2$ and WO$_3$, ZnO and others. Among all nanostructured materials, ZnO is a potential material in various optoelectronic devices [2]. In this study, ZnO is in the form of nanorods because the structure can influence a material to increase the absorption of light caused by its high surface area [3].

ZnO has many advantages that are low-cost in fabrication, high binding energy at room temperature (60 MeV) [4], high stability [5]. However, the disadvantage of ZnO is that it has a wide bandgap value (E$_g$ = 3.37 Ev) [4] so that it is less suitable for application on photodetectors. Therefore, modification is needed. In this study, a modification was carried out by coating Cu$_2$O on the ZnO film. The aim of coating Cu2O is to reduce the bandgap value and increase photoresponse sensitivity so the materials can be suitable for application as a photodetector.
Cuprous oxide (Cu$_2$O) is a $p$-type semiconductor which has a bandgap of about 2.3 eV [6], environmentally friendly (non-toxic), and low-cost fabrication [7], and high optical absorption [8]. So Cu$_2$O has great potential to enhance the performance of ZnO nanorods. The Cu$_2$O fabrication process can also be conducted with simple methods such as Chemical Bath Deposition (CBD). In this study, we investigated the effect of Cu$_2$O coating on ZnO nanorods on phase, morphology, bandgap, and photoresponse.

2. Experimental Method
2.1. The Preparation for ITO substrate
The indium tin oxide (ITO) substrate was soaked in acetone at 50˚C for 15 minutes in an ultrasonic bath. Then, the substrate was leached with deionized water. The pieces of ITO substrate was dried in air.

2.2. Synthesis of ZnO nanoparticle
Zinc Acetate Dihydrate (ZnAc) was dissolved with ethanol to the blended solution. Then the solution was added MEA until pH 4. The solution was stirred for 2 hours. The solution was coated on the cleaned ITO using a spin coater for 30 seconds. After that, the sample was pre-calcined at 150 °C and calcined at 400 °C for 2 hours.

2.3. Synthesis of ZnO nanorods
An amount of Zinc nitrate and hexamethylenetetramine was dissolved in deionized water at room temperature for 50 minutes to the mixed solution. Moreover, the ZnO films were immersed into the solution, and then this solution was heated at 90 °C for 4 hours. After that, the films were calcined at 500 °C.

2.4. Synthesis of Cu$_2$O
An amount of NaOH and water were stirred at 70 °C, called solution A. CuSO$_4$ was dissolved in water, called solution B. Na$_2$S$_2$O$_3$ was dissolved in water, called solution C. Then, solution B and C was totally stirred, called solution D. The ZnO nanorod film was dipped in solution A and D for 20 seconds in sequence (10 times). The films were dried in air.

2.5. Photoresponse Measurement
Photoresponse measurement made with a Keithley model 6517B Source Measure Unit and Labview to drive the source meter. The measurement was carried out in two conditions which are in light conditions and dark conditions. The intensity of the light used in this measurement was 22.1 lux. In this study, the schematics of the photoresponse measurement setup is carried out as in Fig.1.
3. Results and Discussion

Figure 2 presents the XRD patterns of ZnO NRs and ZnO NRs/Cu$_2$O thin films. The diffraction pattern of ZnO nanorods (NRs) matching with PDF number 079-0205. The diffraction peaks of ZnO in Fig. 1a) is at 31.72˚, 34.36˚, 36.18˚, 47.53˚, and 62.86˚, which is according to the literature [5]. The diffraction peaks verify the hexagonal wurtzite ZnO structure. The space group is $P6_3mc$. The diffraction peak of the ZnO layer at 2$\theta$ (34.36) confirms $hkl$ (002). The peak is sharp and strong, it means the orientation of rod growth at the c-axis [6]. Furthermore, we have investigated the morphology using Scanning Electron Microscopy (SEM), presented in Figure 4. For ZnO NRs/Cu$_2$O film in Fig.2b, there are two-phases (ZnO and Cu$_2$O). The diffraction peak of Cu$_2$O is at 36˚, which is according to the literature [7].

For identifying the functional group of the samples, we have characterized using the infrared spectrometer in the range of 400-1100 cm$^{-1}$. In Figure 3, the ZnO films have an absorption peak at 400-500 cm$^{-1}$ and 557 cm$^{-1}$ [8]. Sample A shows a pure phase of ZnO. The Cu$_2$O films have absorption peaks at 618 cm$^{-1}$ (C-O from Cu$_2$O) [9], and 660 cm$^{-1}$ [10], 950 and 1160 cm$^{-1}$ (C-O and C-C) [10], 1508 cm$^{-1}$ [11], 3440 cm$^{-1}$ [11]. Sample B shows two-phases that are ZnO and Cu$_2$O. The absorptions peaks of all samples match with XRD analysis.

The surface morphology of the ZnO films is presented in Fig 4a, and its cross-section is displayed in Fig. 4b. The rods grew vertical to the ITO substrate. But, the rods did totally not grow vertical to the substrate. There are rods growing sideways. The size of the rods was not homogenous and there was much granular. The granular was caused when washing the ZnO film was totally not cleaned. The length of the rod in Fig. 4b is ~ 361 nm. For the sample of ZnO NR/Cu$_2$O in Fig. 4d, the length of the rod is ~ 874.2 nm and the thickness of Cu$_2$O is 21.68 μm. The surface morphology of Cu$_2$O film is like a rectangular cuboid.
Figure 2. XRD pattern of (a) ZnO NRs, (b) ZnO NRs/Cu$_2$O films

Figure 3. FTIR spectra of (a) ZnO NRs and (b) ZnO NRs/ Cu$_2$O
Figure 4. SEM images of (a) ZnO nanorods and (b) cross-section of the film, (c) ZnO nanorods and (c) cross-section of the film

Figure 5 displays the UV-vis absorption of ZnO nanorods without and with Cu$_2$O deposition. The absorption of ZnO nR film is apparent $\sim$ 400 nm and not significant absorbing in visible light range because the sample has a wide energy gap ($\sim$ 3.04 eV), which is according to the literature [12]. The sample of ZnO nR / Cu$_2$O films has an absorbance at $\sim$ 475 nm and the value of band gap energy using Tauc’s plot method shown inset of Fig. 5 is 2.47 eV. The results are a good agreement with the previous reported [13]. The sample of ZnO nR/Cu$_2$O film has a lower bandgap than the ZnO nR film.
Figure 5. UV-Vis absorption spectra of (a) ZnO NR (b) ZnO NR/Cu$_2$O and determination of the bandgap shown in the inset.

The layer arrangement of the samples is shown in Fig. 6a. The process of photoconduction is shown in Fig. 6b. During the light absorption, electron-hole pairs are created \([h\nu \rightarrow e^- + h^+]\) so the electron and holes can get through the depletion layer. When photodesorption section, holes move to the surface to neutralize the negative charge of absorbed oxygen ions \([O_2^- + h^+ \rightarrow O_2]\) [14]. The treatment of Cu$_2$O deposition can influence the result of the photoresponse. The time-dependent response of the photosensor was displayed in Fig. 7. The photoresponse contains two-sections. The first section is photogeneration and recombination of electron-hole pairs, and the second section is surface absorption and photodesorption of oxygen molecules [14].

Figure 6. (a) Configuration of ITO/ZnO NRs/Copper oxide (b) A schematic of charge generation and transfer by lamp illumination

Sample B has a faster response than sample A while the light was on and off. It was caused the Sample B film has a smaller bandgap than Sample A [15]. The quantitative analysis of the rise and decay current in the photoresponse curve that occurs in both samples using the bi-exponential relaxation equation of the following type:

\[
I = I_0 + A \exp\left(-\frac{(t-t_0)}{\tau}\right)
\]

where \(I\) is current as a function of times, \(A\) is constant, \(t\) is time, and \(\tau\) is time rise or decay.
The dashed red line edges between the rise and decays current while the light was on. In sample A (Fig. 7a), the curve shows a slow-response both in the rise and decay current ($\tau_r = 52.97 \text{ s}$ and $\tau_d = 75.95 \text{ s}$). The slow response is caused by trapping electron holes. Sample A has a wide bandgap that can trap the electron thus preventing recombination. Whereas for sample B, when the light on, the curve is sharp and then saturated as shown in Fig. 7b. The same thing occurs when the lights are turned off. It means sample B has a fast response ($\tau_r = 2.75 \text{ s}$ and $\tau_d = 7.58 \text{ s}$). Generally, a fast response is caused by a small bandgap. Sample B has a lower bandgap than sample A. Based on the physical properties described previously, Sample B is more suitable for application in photodetectors than sample A.

![Figure 7. Time-dependent response of the photosensor for (a) ZnO NRs and (b) ZnO NRs/ Cu2O](image)

4. Conclusions
ZnO NR and ZnO NR /Cu2O films have been successfully synthesized. XRD data presented wurtzite phase ZnO matching with PDF number 079-0205. The absorption peaks showed a pure phase for sample A (ZnO) and two-phases in sample B (ZnO and Cu2O) characterizing by FTIR. The morphology of the ZnO films exposes rods in which the rods grew vertical to the ITO substrate in both samples. The bandgap values of ZnO NR and ZnO NR/ Cu2O are 3.04 and 2.47 eV, respectively. From the photosensor measurement, the sample which is coated by Cu2O film was more responsive to the light than the sample ZnO NR without coating Cu2O. For photodetector application, coating Cu2O film on ZnO NR is better than without coating Cu2O.

5. References
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**Acknowledgments**

This research was also supported by the Ministry of Research Technology and High Education of the Republic of Indonesia awarded to Nandang Mufti.