Investigation of optical properties of hybrid ZnO/Graphene-based photodetectors

N Sholeha\(^1\), K D Lestari\(^1\), I Zulianti\(^1\), A A Ittikhad\(^1\), N A Sofa\(^4\), N Mufti\(^{1,2}\), and R Kurniawan\(^{1,2,*}\)

\(^{1}\)Department of Physics, Faculty of Mathematics and Natural Sciences, Universitas Negeri Malang, Jl. Semarang 5, Malang 65145, East Java, Indonesia
\(^{2}\)Centre of Advanced Materials for Renewable Energy (CAMRY), Universitas Negeri Malang, Jl. Semarang 5, Malang, 65145, East Java, Indonesia

*Corresponding author: robi.kurniawan.fmipa@um.ac.id

Abstract. The problem of ozone depletion lies behind the importance of developing a photodetector device, which is used as a preliminary detection step against the risk of solar radiation. At present, hybrid photodetectors are a major concern because they have detection and operational advantages over conventional photodetectors. In this study, we investigated the optical properties and photoresponse of hybrid ZnO/graphene (HZG) systems, of which ZnO nanorod (ZnO NR) was used in the system. Investigations were carried out using spectroscopic ellipsometry (SE) and solar simulators. The results of SE fittings with the effective medium approximation (EMA) method confirmed that the length of ZnO NR was 27.81, 42.67, and 220.46 nm respectively. We note that increasing the size of ZnO NR promotes light absorption to increase significantly. Furthermore, the relationship between light absorption and HZG photoresponse was discussed using a comprehensive analysis.

1. Introduction

ZnO is a semiconductor material from groups II-VI that promises to be a photodetector device because it has good radiation strength and high chemical stability. ZnO has a bandgap of around 3.3 eV at room temperature (300 K) [1-2,13-16]. Changes in the bandgap can occur if there are changes in temperature and pressure. ZnO has exciton binding (60 meV) which is greater than its thermal energy (26 meV), its excitation and emission are effective at room temperature [3-5].

Previous research was conducted by Yang by making ZnO nanowire as a UV photodetector which can show UV response very well. Other studies conducted by Liu et. al and Boruah et.al, both add graphene to the ZnO system. Graphene was chosen because it has good carrier mobility and electrical conductivity. However, until now, the development in terms of detection, responsivity, and change in gain is a challenge that must be faced in the mass structure so that in this study we are incorporating ZnO/Graphene hybrid material, which is thought to be used to improve photodetector performance.

Graphene is a two-dimensional material with carbon atoms arranged in a honeycomb-shaped lattice [6-7]. Recently, graphene has received special attention for many applications due to its high carrier transport mobility and excellent electrical conductivity [6]. Besides being known to have unique electrical and optical properties of graphene has an abundant amount in nature, so it has the opportunity to be continuously developed [2].
In this study, we investigated the optical and photoresponsive properties of hybrid ZnO NR/Graphene (HZG). There are several methods to deposit the solution, i.e chemical bath deposition [9], electrodeposition [10], doctor blade deposition [11], and chemical vapor deposition [12]. The hydrothermal and simple-spray deposition were carried out during HZG synthesis by varying the time spraying of ZnO NR with the various time of 3, 20, and 40 seconds that affects the length of ZnO NR. This method was chosen because the method is simple and low cost. This investigation was carried out using spectroscopic ellipsometry (SE) and photoresponse to observe the light absorption and photoresponses from HZG. Light absorption is one of the important parameters for the photodetectors because the impression of photodetector performance can be reached if the semiconductor has a significant extinction coefficient gathered with a high photovoltage [8]. The results of the investigation of the optical properties and photoresponse of HZG will provide knowledge in increasing the effectiveness of the photodetector.

2. Methods
An ITO-glass substrate was cleaned with ethanol and sonicated for 10 minutes. Then, cleaned again with deionized water and sonicated again at the same time before. Graphene was dissolved in 20 ml ethanol and was deposited on the ITO-glass substrate using a spray method with a diameter of 300 nm. The ZnO seed solution was prepared using Zn(CH$_3$COO)$_2$.2H$_2$O in 20 ml of ethanol. The solution was stirred at 100 °C, 300 rpm for 45 minutes. The ITO-glass/Graphene was placed on a hotplate at 150 °C and sprayed the ZnO seed at a distance of 14 cm for various times of 20 and 40 seconds. This process produces a thin film of hybrid ZnO/Graphene (HZG) system. Zn(NO$_3$)$_2$.4H$_2$O and (CH$_2$)$_6$N$_4$ dissolved in 50 ml of deionized water. The solution was stirred at room temperature, 400 rpm for 45 minutes. The solution was prepared for ZnO NR growth on the HZG systems using a hydrothermal method. The ITO-glass/Graphene/ZnO soaked into the solution for 3.5 hours at a solution temperature of 90 °C. The samples were cleaned using deionized water and annealed at 100 °C for 3 minutes. The samples with the codes for each time variations 3, 20, and 40 seconds namely ZnO, ZGR-1, ZGR-2, respectively. The optical properties were characterized by using spectroscopic ellipsometry (SE). The photoresponse was measured for voltage vs time ($V$-$t$) by Keithley 6515B Electrometer under illumination of 20 mW/cm$^2$ light.

3. Results and Discussion
The investigation of the optical properties of the sample was performed by measuring changes in polarized light in the sample so that the $\Psi$ (related to polarization) and $\Delta$ (related to absorption) spectra are produced. Figure 1 shows that the ZGR-2 sample has the greatest change in $\Psi$ and $\Delta$, in other word, it has higher absorption than that of the other samples. The $\Delta$ spectrum shows significant changes in intensity in the range of 1.5-3.5 eV, which indicated the band gap of ZnO. In this range, the electron excitation process is possible from the valence band to the excitation state due to the absorption of energy from photons. The effect of adding graphene has an impact on the optical parameters that are being discussed. Obtaining information related to the length of ZnO NR is obtained using the effective model approximation (EMA) fitting. Here, the obtained lengths are 27.81, 42.67, and 220.4 nm.

The relationship between the extinction coefficient ($k$) and photon energy is showed in Figure 2. The extinction coefficient is proportional to $\varepsilon_2$, which represent light absorption according to the following Equations [17]:

\[
\varepsilon = \varepsilon_1 - i\varepsilon_2 \quad (1)
\]

\[
\varepsilon_1 = n^2 - k^2 \quad (2.a)
\]

\[
\varepsilon_2 = 2nk \quad (2.b)
\]
Figure 1. Spectroscopic ellipsometry spectra; amplitude ratio $\Psi$ (a) and phase difference $\Delta$ (b) of HZG systems and extinction coefficient $k$ (c) and absorption coefficient $\alpha$ (d) of the samples.

Besides, if we use equation (2) with $k = 0$ when there is no light absorption, the complex refractive index is given by [17]:

$$n = \left\{ \frac{\varepsilon_1 + \left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2}}{2} \right\}^{1/2}$$  \hspace{1cm} (3.a)

$$k = \left\{ \frac{-\varepsilon_1 + \left(\varepsilon_1^2 + \varepsilon_2^2\right)^{1/2}}{2} \right\}^{1/2}$$  \hspace{1cm} (3.b)

Based on Figure 1(c), the extinction coefficient increases as the length of ZnO NR increase, where the $k$ of ZGR-2 is higher than that of the other samples. Based on these results, the highest intensity of $k$ is in the range of 2.6 - 3.0 eV, where the energy in that range smaller than the ZnO bandgap energy (~ 3.37eV). Figure 1(d) shows the optical absorption coefficient which value was not constant and depends on the energy of the electromagnetic waves absorbed by the material. Optical constants play an important role in planning optoelectronic device schemes because they are related to the electronic polarization of ions and local fields in materials [18]. The extinction coefficient $k$ is related to the absorption coefficient ($\alpha$) by following Equation [17]:

$$\alpha = \frac{4\pi k}{\lambda}$$  \hspace{1cm} (4)
The results show that the highest optical absorption coefficient is owned by ZGR-2 at photon energy range of 1.4 - 3.5 eV. The high optical absorption coefficient on ZGR-2 indicates that the material can absorb more photons due to interaction of electrons when moving from one band to another band. The addition of graphene on ZnO promotes the increase of optical absorption coefficient. The peak at 3.5 eV is related to the UV light absorption.

The photoresponse factor is one of the parameters considered as an established factor of high performance of photodetectors. In this study, the ON and OFF time was maintained for the span time of 40 seconds.

![Figure 2](image)

**Figure 2.** *V*-*t* graph of the samples; (a) ZnO, (b) ZGR-1, and (c) ZGR-2.

Figure 2(a), 2(b), and 2(c) indicate the photoresponse of the samples through *V*-*t* measurement of ZnO, ZGR-1, ZGR-2, respectively. Generally, ZnO, ZGR-1, ZGR-2 show a good response to the light condition when on and off. The best photoresponse showed by ZGR-1 which has a fast response when the light was controlled while ZnO and ZGR-2 have a slower response than ZGR-1. Photodetector response of the nanostructure with a light illumination can be explained by desorption and adsorption of O\textsubscript{2} and/or H\textsubscript{2}O on its surface [19-23]. In dark conditions, O\textsubscript{2} and H\textsubscript{2}O molecules present in the air are adsorbed on the ZnO surface and it affects the increasing depletion barrier height [24]. When the light is turned on, the chemisorbed O\textsubscript{2} gets H\textsubscript{2}O is/are desorbed in two ways; (i) capturing the photo-generated hole and/or (ii) direct photo-excitation of a captured electron to the conduction band of ZnO [25].
4. Conclusion

We have proposed the simple and inexpensive method for preparing HZG, namely the spray and hydrothermal method. The results of SE fittings with the effective medium approximation (EMA) method confirmed that the length of ZnO NR was 27.81, 42.67, and 220.46 nm respectively. Different length of ZnO NR in each sample shows significant changes to physical quantities such as the extinction coefficient $k$, absorption coefficient $\alpha$. The photoresponse of HZG systems shows a good response through light on and off condition. These changes can be used as a basis for the development of UV photodetector where HZG responsiveness has a good response in the range of UV light energy.

References
[1] N. Mufti, S. Maryam, A. A. Fibriyanti, R. Kurniawan, A. Fuad, and A. Taufiq, “Morphological Modification and Analysis of ZnO Nanorods and Their Optical Properties and Polarization,” vol. 2018, 2018.
[2] S. Biswas, P. Sharma, V. Awasthi, and B. S. Sengar, “Photosensitive ZnO-Graphene Quantum Dot Hybrid Nanocomposite for Optoelectronic Applications,” pp. 1503–1509, 2016.
[3] Y. Ning, Z. Zhang, F. Teng, and X. Fang, “Novel Transparent and Self-Powered UV Photodetector,” vol. 1703754, 2018.
[4] B. D. Boruah, D. B. Ferry, A. Mukherjee, and A. Misra, “Few-layer graphene / ZnO nanowires based high performance UV photodetector,” Nanotechnology, vol. 26, no. 23, pp. 1–7.
[5] S. Chang and K. Chen, “Zinc Oxide Nanoparticle Photodetector,” vol. 2012, pp. 1–6, 2012.
[6] V. Q. Dang et al., “Ultrahigh Responsivity in Graphene – ZnO Nanorod Hybrid UV Photodetector,” no. 25, pp. 3054–3065, 2015.
[7] B. Y. Zhang et al., “Broadband high photoresponse from pure monolayer graphene photodetector,” Nat. Commun., vol. 4, no. May, p. 1811, 2013.
[8] D. Banerjee and K. K. Chattopadhyay, Hybrid Inorganic Organic Perovskites: A Low-Cost-Efficient Optoelectronic Material. Elsevier Inc., 2018.
[9] Al-asadi, A. S. et al. (no date) ‘Fabrication and Characterization of UV Photosensors from ZnO Nanowires Prepared Using Chemical Bath Deposition Method’.
[10] Abd-ellah, M. et al. (2016) ‘Solar Energy Materials & Solar Cells Enhancement of solar cell performance of p-Cu 2 O / n-ZnO-nanotube and nanorod heterojunction devices’, Solar Energy Materials and Solar Cells. Elsevier, 152, pp. 87–93. doi: 10.1016/j.solmat.2016.03.022.
[11] Azarang, M. and Sookhakian, M. (2015) ‘RSC Advances response and optical properties of reduced graphene oxide uniformly decorated zinc oxide nanoparticles based on the graphene oxide concentration’, RSC Advances. Royal Society of Chemistry, 5, pp. 53117–53128. doi: 10.1039/C5RA06123G.
[12] Boruah, B. D. et al. (no date) ‘Few-layer graphene / ZnO nanowires based high performance UV photodetector’, Nanotechnology. IOP Publishing, 26(23), pp. 1–7. doi: 10.1088/0957-4484/26/23/235703.
[13] L. Luo, Y.F. Zhang, S.S. Mao, L.W. Lin, Fabrication and characterization of ZnO nanowires based UV photodiodes, Sens. Actuators A 127 (2006) 201–206.
[14] HuangMH, Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R and Yang P 2001 Science 292 1897–9.
[15] P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He and H.-J. Choi, Adv. Funct. Mater., 2002, 12, 323.
[16] K. C. Park, D. Y. Ma and K. H. Kim, Thin Solid Films, 1997, 305, 201–209.
[17] Fujiwara, H. (no date) SPECTROSCOPIC Principles and Applications.
[18] Talib, R. A. et al. (2016) ‘Effect Of Growth Time On Structure , Optical And Photo- Response Characteristics Of ZnO Nanorods Deposited Onto Various Substrates’, 12(3), pp. 171–184.
[19] S. Chang and K. Chen, “Zinc Oxide Nanoparticle Photodetector,” vol. 2012, pp. 1–6, 2012.
[20] V. Q. Dang et al., “Ultrahigh Responsivity in Graphene – ZnO Nanorod Hybrid UV
Photodetector,” no. 25, pp. 3054–3065, 2015.

[21] B. Y. Zhang et al., “Broadband high photoresponse from pure monolayer graphene photodetector,” Nat. Commun., vol. 4, no. May, p. 1811, 2013.

[22] D. Banerjee and K. K. Chattopadhyay, Hybrid Inorganic Organic Perovskites: A Low-Cost-Efficient Optoelectronic Material. Elsevier Inc., 2018.

[23] Chen, Q. et al. Passivation of surface states in the ZnO nanowire with thermally evaporated copper phthalocyanine for hybrid photodetectors. Nanoscale 5, 4162–4165 (2013).

[24] Law, J. B. K. & Tong, J. T. L. Simple fabrication of a ZnO nanowire photodetector with a fast photoresponse time. Appl. Phys. Lett. 88, 13–15 (2006).

[25] Yan, C., Singh, N. & Lee, P. S. Wide-bandgap Zn2GeO4 nanowire networks as efficient ultraviolet photodetectors with fast response and recovery time. Appl. Phys. Lett. 96 (2010).

**Acknowledgment**

This research was supported by PNBP 2019 research program from Universitas Negeri Malang.