Optical and Morphological Properties of ZnO Nanostructure by Coating Aluminium and Plasmonic Material

Rinaldo Abdi¹, Romi F Syahputra¹, Ridho Kurniawan² Awitdrus³, Iwantono³*

¹Graduate student of master of physics, Universitas Riau, Pekanbaru—Indonesia
²Baristand Industri Banda Aceh—Indonesia
³Senior lecturer of physics department, Universitas Riau, Pekanbaru—Indonesia

Corresponding e-mail: iwantono@lecturer.unri.ac.id

Abstract. We provide a preliminary study of ZnO nanostructure synthesis by coating aluminium and metallic plasmonic Au-Ag using seed mediated hydrothermal method. The growth process is carried out on the FTO substrate and characterized using UV-Vis, XRD, FESEM and EDX spectrophotometer system. The UV-Vis spectrum shows that strong absorption occurs at wavelengths around 370 nm, for all samples. The XRD pattern shows three diffraction peaks at angles 2θ = 34.43°, 36.32° and 47.49°. Each peak corresponds to the crystal fields of (100), (002) and (101). Morphology of the samples shows the presence of ZnO nanorod. A compact and denser nanostructure also obtained.

1. Introduction
ZnO as a semiconductor material attracting attention of the researchers because its advantages in developing many devices, such as energy harvester [1-3], biosensor [4,6], medical devices [5,6], and electronic devices [7,8]. Bulk ZnO has a large enough energy gap, which is 3.34 eV, so that it is transparent in the visible light on the electromagnetic spectrum [8]. Furthermore, ZnO has a cheap and a flexible base material also makes it is easy to be deposited on other layers or substrates. The growth of ZnO nanorods can be done by various methods, one of them is by seed mediated hydrothermal method [9,10].

As effort to improve the physical properties of ZnO nanorod, doping process is carried out by some dopants. This treatment aims to increase conductivity and mobility of ZnO nanostructures, as well as to obtain transparency, stability and high conductivity [11]. The addition of metal atoms such as aluminum (Al) can improve the physical properties of ZnO nanorods [12]. Aluminum coating on the ZnO layer can reduce ZnO particle size, increase transparency in visible regimes and increase the conductivity [12].

The addition of plasmonic material, such gold (Au) and silver (Ag) [13,14], into ZnO growth can enhance it electrical properties. Ag and Au metals have good chemical stability and high conductivity so that a density of electron can achieve [15-17]. In this paper, we provide a technique to obtain ZnO nanorod on fluorine-doped tin oxide (FTO) substrate with aluminium-coated and plasmonics by a simple method, namely seed mediated hydrothermal. We also give their optical and morphological properties The objective of this research is to obtain high-quality ZnO nanomaterials which can be applied to various fields, especially for dye sensitized solar cells (DSSCs) and biochemical sensing.
2. Method
The initial step of this study is to wash synthesis bottles and FTO glass. Then a seeding and growing the nanostructure is straightforward accomplished. The last process is characterization of the sample using UV-Vis, XRD, and FESEM.

2.1. Seedling and growing ZnO
The seeding is obtained by dissolving 32.9 g of ZAD powder into 15 mL ethanol and dissolved by ultrasonic bath for homogeneous solution. Then, 200 µL seedling solution is dispersed on the FTO surface by spin coater for 30 seconds at rate of 3000 rpm. The sample is heated on a hot plate for 15 minutes at 105°C. The same process is repeat for three times to achieve a compact nanostructure [10,11]. Annealing is applied for 1 hour at 350°C using furnace. This annealing process aims to eliminate other elements that are attached to the substrate. A growth process starts by making two solutions of 0.1 M ZNH and 0.1M HMT into 10 mL DI water, respectively, then mix both solution in one bottle. The seedling sample is immersed into the mixture with oblique position and oven at 90°C for 8 hours. As final growing step, the sample is cleaned using DI water.

2.2. Aluminium coating
Aluminium coating is carry out by immersion method at room temperature for 30 minutes. 112.5 mg of aluminum nonahydrate nitrate is added into 3mL of DI water and dissolved using an ultrasonic bath until homogeneous solution of 0.1M prime aluminium solution is obtained. For immersion solution, only 2% of the prime solution to dilute 20mL aluminium solution. The sample is inserted horizontally into synthesis bottle for the coating process, then aluminum immersion solution is put into the synthesis bottle using a dropper. This immersion process is carried out at the least for 30 minutes at room temperature. After preparation of the sample is done, rinsed using DI water slowly and placed on a petri dish, dried in an oven at 100°C for 10 minutes.

2.3. Plasmonic coating
Plasmonic coating is carried out by spin coat method for 15 times. This process starts by making Au and Ag solution from mixture of 0.5 mL HAuCl₄/trisodium citrate and AgNO₃/trisodium citrate into 20 mL DI water, respectively. The solution is then hushed up for 30 minutes and put 0.1 M NaBH₄ (in a cold state) into the solution. Au coating will be firstly accomplished and then followed by Ag coating for 10 seconds at speed rate of 1000 rpm.

3. Results and Discussions

3.1. Optical properties
The UV-Vis absorption spectrum in Fig. 1 shows the optical absorption spectrum of the samples namely pure ZnO, ZnO+Al, ZnO+Al+Ag and ZnO+Al+Au. The spectrum shows that strong absorption occurs in the wavelength range of 300-400 nm. The absorption rate of the sample rises after coadde by plasmonic layer, this is because after the addition of the plasmonic, the sample becomes less transparent, so more ZnO nanostructures are involved in the process of absorbing light [12]. Decreasing absorption of other samples caused the ZnO formation is more roughly so that photon scattering is more occurring [13].
Each sample has three peak diffractions appearing at an angle of $2\theta = 34.43^\circ$, $36.62^\circ$ dan $47.49^\circ$ as depicted in Fig. 2. These peak corresponds to the crystal plane (100), (002) and (101) which indicate that crystalline structure is obtained. The highest diffraction peak at $34.43^\circ$ shows compact form of ZnO nanorod [14].

3.2. Morphological properties

Figure 3 shows show morphology of the samples, where ZnO nanomaterials arranged in the form of nanorods with a hexagonal cross section. The presence of Al, Ag and Au in the ZnO structure is
seen to influence the shape of the ZnO and a denser nanostructure is achieved. Moreover, dominant width of the nanostructure also increase, namely pure ZnO ~100 nm, ZnO+Al ~125 nm, ZnO+Al+Ag ~130 nm and ZnO+Al+Ag ~150 nm. The nanorod is also seen to be overlapped because their orientation is not vertically aligned to the FTO [15].

![Surface morphology of the samples in 50,000 magnification. A) Pure ZnO, B) ZnO+Al, C) ZnO+Al+Ag, and D) ZnO+Al+Au.](image)

4. Conclusion

Al-coated ZnO nanorod which coated by Ag-Au plasmonic was successfully grown on top of the FTO. The results of UV-Vis characterization showed that the peak of strong absorption of samples occurred in the wavelength range of 300-400 nm for all samples. Diffraction peak with the highest intensity occurs at angle of 2θ=34.43° which is more dominant than other diffraction peaks. By Al and plasmonic coated, a compact and denser ZnO nanostructure is achieved. Dominant width of the nanostructure also rise significantly.

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References

[1] Si H, Kang Z, Liao Q, Zhang Z, Zhang X, Wang L and Zhang Y 2017 Sci. China Mater. 60 793-810.
[2] Chen X, Tang Y and Liu W 2017 Molecules 22 1284(1-6).
[3] Winantyo R and Murakami K 2017 Int. J. Technol. 8 1462-1469.
[4] Ahmad R, Tripathy N, Ahn M S and Hahn Y B 2017 Sci. Rep. 7 46475 (1-8).
[5] Chung R J, Wang A N, Liao Q L and Chuang K Y 2017 Nanomaterials 7 36(1-10).
[6] Zhang H, Zhang M, Lin C and Zhang J 2018 Sensors 18 218(1-10).
[7] Ridhuan N S, Abdul-Razak K and Lockman Z 2018 Sci. Rep. 8 13722(1-12).
[8] Mohammed A M, Ibraheem I J, Obaid A S and Bououdina M 2017 Sens. Bio-Sens. Res. 15 46-52.
[9] Dixit T, Palani I A and Singh V 2018 RSC Adv. 8 6820-6833.
[10] Zhang Y, Ram M K, Stefanakos E K and Goswami D Y 2012 J. Nanomater. 2012 624520.
[11] Graetzel, M J 2004 J. Photochem. Photobiol., A, 164., pp 3-14
[12] Kim S Y, Lee K H, Chin B D, Yu and J W 2009 Sol. Energy Mater. Sol. Cells 93 129-35.
[13] Wang W, Ai T and Yu Q 2017 Sci. Rep. 7 42615(1-11).
[14] Lin S S, Huang J L and Saigalik P 2004 Surf. Coat. Technol. 185 254–263.
[15] Mostafaei A and Zolrasatein A 2012 Prog. Nat. Sci.: Mater. Int. 22 273-80.
[16] Rahman M Y A, Umar A A, Roza, Samsuri S A M, Salleh M M, Iwantono and Tugirin 2015 J. New Mater. Electrochem. Syst. 18 8-16.
[17] O’Regan B and Graetzel M 1991 Nature 353 737-40.
[18] Graetzel M 2003 Nature 414 338–44.
[19] Nelson J 2003 *The Physics of Solar Cells* (Imperial College Press, London, UK).

[20] Iwantono I, Nurwidya W, Lestari L R, Naumar F Y, Nafisah S, Umar A A, Rahman M Y A and Salleh M M 2015 *J Solid State Electrochem.* **19** 1217–21.

[21] Iwantono I, Tugirin S, Anggelina F, Awitdrus, Taer E, Roza L and Umar A A 2016 *AIP Conf. Proc.* **1712** 050024.

[22] Umar A A, Rahman M Y A, Taslim R., Salleh M M, and Oyama M 2011 *Nanoscale Res. Lett.* **6** 564.

[23] Wang J, Sun X W, Jiao Z 2010 *Mater.* **3** 5029-53.

[24] Qian X, Liu H, Guo Y, Song Y, Li Y 2008 *Nanoscale Res. Lett.* **3** 303-307.

[25] Bora T, Kyaw H H, Sarkar S, Pal S K, Dutta J 2011 *Beilstein J. Nanotechnol.* **2** 681-90.

[26] Bora T, Zoepfl D, Dutta J 2016 *Sci. Rep.* **6** 26913.