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THE SYNTHESIS AND CHARACTERIZATION OF ZINC OXIDE THIN FILM DOPING SELENIUM

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ABSTRACT

The selenium-doped ZnO nanomaterial has successfully grown the surface of FTO (Fluorine Tin Oxide) using a seed-mediated hydrothermal method at a temperature of 90°C for 5 hours. In this research, the doping selenium by variation the volume of selenium solution at 0 mL, 0.025 mL dan 0.2 mL. This is an impact on the optical properties and morphology of ZnO nanorods. The samples were characterized using UV-Vis spectroscopy, X-Ray Diffraction and Field Emission Scanning Electron Microscopy (FESEM). The UV-Vis spectra showed that strong absorption occurs in the wavelength range of 300-380 nm. The 0.025 mL Se doped ZnO was the highest absorption compared to other samples. The XRD pattern exhibited five peaks at an angle of 2 θ : 31.70°; 34.4°; 36.2°; and 47.5°. representing the orientation of the crystal planes (100), (002), (101), and (102) of hexagonal lattice. The FESEM images showed that Se doped ZnO with hexagonal face shape. The 0.2 mL Se doped ZnO was the most uniform compared to other samples.

Keywords: selenium doped ZnO nanorods, seed-mediated hydrothermal method, UV-Vis, XRD, FESEM

INTRODUCTION

The majority of the world's energy needs rely on fossil fuels in the form of petroleum whose reserves are dwindling. The use of fossil materials also has a negative impact from harmful gas emissions that result in environmental pollution [1]. Therefore, it is necessary for alternative renewable energy sources and environmentally friendly to meet the world's energy needs. One of the alternative energies that can be renewed as a substitute for fossil materials is solar cells, which are capable of converting solar energy into electrical energy without producing any exhaust gases or free of carbon [2].

In recent years, materials technology has developed so rapidly. It is ranging from large-scale material to the smallest one. Many methods are used to produce the desired material properties for specific applications. Nanostructured material made from semiconductors is widely studied because it has good transparency properties, and many applications [3]. In solar cell application, a semiconductor material that is commonly used are ZnO and TiO₂. Nowadays, ZnO is preferred because it has a large surface area, electrons mobility, more easily produced in unique nanostructures, and low cost of fabrication [4].

The addition of metal or non-metal atoms to ZnO (doping) is commonly done to optimize the properties of a material. ZnO can be doped with different types of metals such as aluminum and gallium [5], and non-metals such as Sulfur and Nitrogen. Non-metallic elements were used as doping because they are more electronegative and more easily attract valence electrons from other atoms.

ZnO semiconductor doping using elemental Se (Se-ZnO) has the potential ability to increase efficiency, but it is still very rare. Xu et al. reported the incident photoelectric conversion efficiency of the photo to current efficiency (IPCE) PSC increased by 27% after Se doped ZnO pure, from 6.65% to 8.44% through the process of synthesis using methods silar (successive ion layer adsorption and reaction) [6]. However, this method requires complicated equipment, and the synthesis conditions are difficult. In this research, the synthesis of Se doped ZnO nanorod thin films was carried out on using the seed-mediated hydrothermal method is simpler and easier. A thin layer of ZnO doped with Se (Se-ZnO) was then applied as ETM to solar cells. The optical, structure and morphology of ZnO nanorods thin films were characterized using UV-Vis spectroscopy, X-Ray Diffraction and Field Emission Scanning Electron Microscopy (FESEM), respectively.

METHOD

Seeding Process of ZnO nanorod

The seeding process is carried out before the process of growing to produce seeds that will grow on top of the substrate. Zinc acetate dihydrate (ZAD) 0.01 M solution in 10 ml absolute ethanol was used as a seeding solution. Next, the ZAD solution was deposited on the substrate using a spin coater at 3000 rpm for 30 seconds. The sample was then heated on a hot plate at 100°C for 15 minutes. This process was repeated three times. Finally, the sample is annealed at 275°C for 1 hour.

Growth Process of Se-ZnO Nanorods

The ZnO nanomaterial growth solution was made by mixing 0.1 M of ZNH (zinc nitrate hexahydrate) solution and 0.1 M of HMT (hexamethyl tetramine) solution. The doping process was carried out simultaneously with the growth solution of ZnO nanomaterials. The main element of doping consists of sodium borohydrate (NaBH_4) and selenium powder. The doping solution was prepared by adding 0.0378 grams of NaBH_4 into dissolved 0.0378 grams of selenium powder in 10 mL DI water. The growth solution was put into a synthesis bottle, then the volume of the doping solution was added, namely 0 mL, 0.025 mL, and 0.2 mL. Then the substrate was hung in a synthesis bottle to form an angle of 90° . The bottle was then put in the oven for 5 hours at 90°C . Samples were afterward rinsed using DI Water and dried. Next, the sample was annealed at 275°C for 1 hour. Finally, samples were characterized using UV-Vis Spectroscopy, XRD, and FESEM.

RESULT AND DISCUSSION

The absorption spectrum of ZnO and Se-ZnO nanomaterial samples is shown in FIGURE 1. It is seen that strong absorption occurs in the wavelength range of 300-380 nm, whereas weak absorption occurs at wavelengths of 380-800 nm for all samples. The lowest intensity of the absorption belongs to the 0.2 mL Se-ZnO sample, while the highest absorption intensity belongs to the 0.025 mL Se-ZnO sample. This event is in accordance with research from Wang, which reported that the strong absorption of the ZnO thin layer occurs in the ultraviolet (UV) wavelength range, while weak absorption occurs in the visible range (visible light) [7]. Visible light wavelengths have weak absorption indicating the characteristics of the ZnO semiconductor [8]. The increase in absorption intensity in the 300-380 nm wavelength range results in electrons from the sample being excited from a low energy level to a higher energy level, while a decrease in absorption intensity does not have sufficient energy to be able to excite an electron from a lower energy level to a higher energy level. If a sample has a high absorbance value, it can be said to be one of the optical properties that can be applied to solar cells.

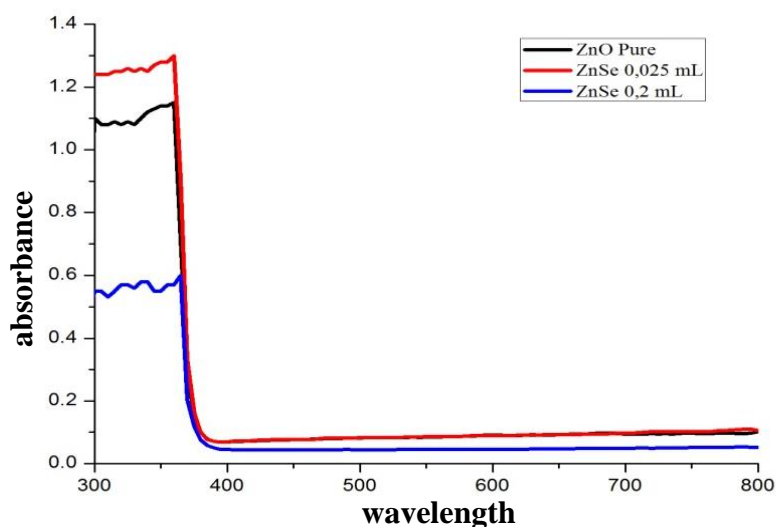


FIGURE 1. UV-Vis absorption spectrum in ZnO and Se-ZnO samples.

The UV-Vis spectrum not only provides information about the absorption rate of the sample, but also provides information regarding optical properties such as the energy gap shown in TABLE 1.

TABLE 1. Energi gap nanorod ZnO *Pure* dan Se-ZnO

No.	Samples	Energy Gap (eV)
1	ZnO <i>Pure</i>	3.29
2	Se-ZnO 0.025 mL	3.28
3	Se-ZnO 0.2 mL	3.26

Based on TABLE 1, pure ZnO nanomaterials have an energy gap of 3.29 eV. The energy gap decreases with the increase in the volume of the doping solution (atomic percent Se/ZnO). The 0.2 mL Se-ZnO sample had the lowest energy gap, which was 3.26 eV. A small decrease in the energy gap indicates the emergence of additional energy bands from the doping element into the ZnO conduction band and due to the low energy gap of Se-ZnO \sim 2.7 eV [9]. The reduced width of the valence bandgap to the conduction band indicates that more electrons undergo electronic transitions from the valence band to the conduction band [10].

The XRD pattern of the ZnO nanomaterial doped with Selenium (Se) is shown in FIGURE 2. From the XRD data, it appears that five peaks of the detected structure diffraction peaks were detected at an angle of $2\theta = 31.70^\circ$; 34.30° ; 36.25° ; and 47.59° . Which corresponds to the hkl fields (100), (002), (101), and (102), which has a hexagonal structure with a lattice parameter ratio c/a is 1.6. The orientation diffraction peak (002) is the highest peak, which is the peak characteristic of ZnO.

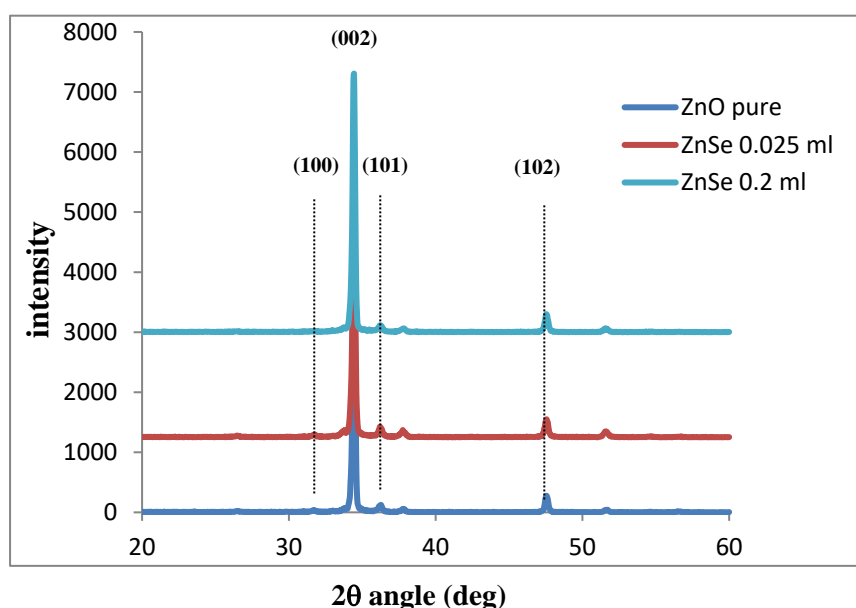


FIGURE 2. XRD pattern of ZnO nanorod pure and Se-ZnO nanorod.

The results of FESEM scanning from ZnO and Se-ZnO samples are displayed with a magnification of 30,000 times seen in FIGURE 3. FESEM photos show that the grown ZnO and Se-ZnO nanomaterials are nanorod-shaped with hexagonal cross-sections. The ZnO surface is covered by doping with Selenium. The distribution of particles or rods is more evenly and densely after supporting, which means that the rod grows more and more tightly. The Se-ZnO 0.2 mL sample looked more uniform than the other samples. Wang states that there is an increase in nanomaterial growth due to an increase in the concentration and volume of its precursors [11]. Overall in the figure shows that all nanomaterial Se-ZnO nanorod form which has been synthesized and has the shape of a hexagonal structure as has been confirmed in XRD measurements.

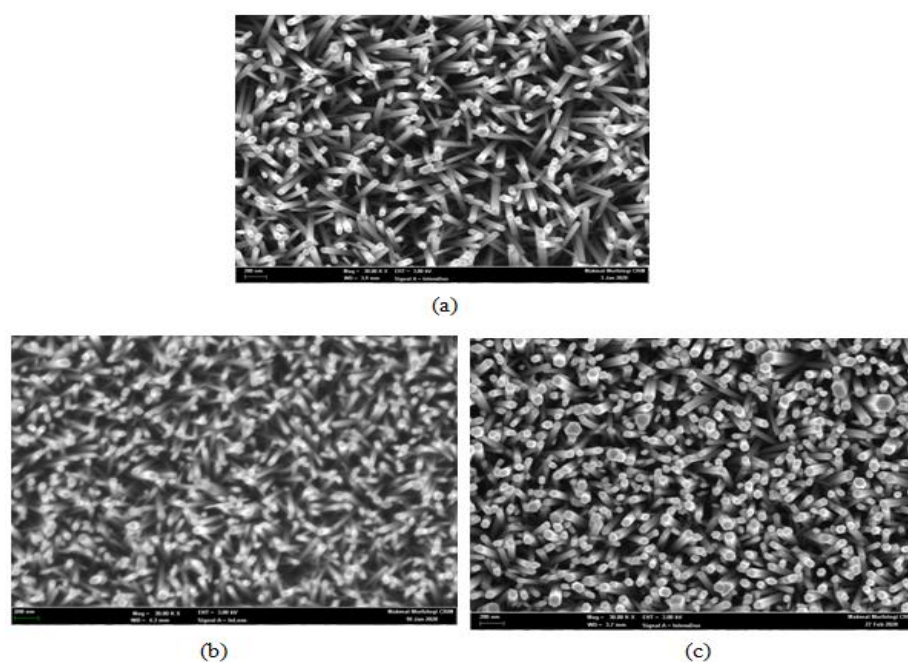


FIGURE 3. Photo FESEM (a) Pure ZnO, (b) 0.025 mL Se (c) 0.2 mL Se.

CONCLUSION

Based on the analyzed research results, it can be concluded that the Se-ZnO nanomaterial has been successfully grown on the FTO with variations in the volume of the Se solution, i.e., 0 mL, 0.025 mL, and 0.2 mL, using the seed-mediated hydrothermal method for 5 hours at 90°. This doping has a positive effect on the growth of ZnO nanomaterials according to their optical and morphological properties of the samples. The absorption spectrum results showed that the strong absorption occurs at a wavelength of 300-380 nm, where the 0.025 mL Se-ZnO sample has the highest absorption intensity. The XRD pattern showed that the crystal structure formed is hexagonal with the lattice parameter ratio c/a is 1.6. The FESEM photo showed the Se-ZnO nanomaterial having a nanorod shape with a hexagonal structure. It can be seen in pure ZnO nanorods that there are still many parts of the FTO that are not covered by ZnO nanorods, and the direction of ZnO nanorods that grows is more inclined. As the percentage volume of selenium increases, the presence of other elements is more visible, which is denser and more regular.

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