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SEED MEDIATED SYNTHESIS OF HEXAGONAL S-DOPED ZnO NANOROD AND ITS PHYSICAL PROPERTIES

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ABSTRACT

Sulfur-doped zinc oxide (S-ZnO) nanorod has been successfully synthesized via the seed-mediated hydrothermal method with different sulfur concentrations (0%, 1%, 2.5%). This research aims to study the influence of the concentration of sulfur on the structure, morphology, and optical properties of ZnO as a promising material in a wide range of applications. Crystal structure, morphology, and optical properties of the samples were characterized using X-Ray Diffraction (XRD), Field Emission Electron Scanning Microscopy (FESEM), and UV-Vis Spectroscopy, respectively. The XRD pattern shows the strongest peak at $2\theta = 34.43^\circ$ for crystal orientation of (002). The crystallinity properties of the S-ZnO sample are higher compared to the ZnO sample. The FESEM images of the 1% S-ZnO sample exhibit the highest nanorod density arrangement. The optical absorbance of the higher sulfur dopant possesses a higher optical absorption peak on the UV-Vis spectrum. The results indicate that S doping to ZnO can alter the structural, morphological, and optical properties of ZnO.

Keywords: ZnO nanorod, sulfur doping, hexagonal, seed-mediated hydrothermal

INTRODUCTION

ZnO (zinc oxide) with one-dimensional (1-D) nanostructures have attracted much attention in recent years due to its wide potential applications. The potential applications of ZnO nanostructures have been popular in various areas such as solar cells [1], photocatalysis [2], piezoelectric [3], biosensors, and gas sensors [4]. Zinc oxide is a combined semiconductor of IIB-VIA with an energy band gap of 3.37 eV and an exciton binding energy of 60 meV. This binding energy is more significant than thermal energy at room temperature, making it applied in UV-blue light emission and room temperature UV amplifiers [5]. ZnO semiconductors are materials that have excellent chemical and thermal stability and are environmentally friendly. ZnO research is still being developed to obtain an optimum optical, electrical, and structural property for a particular application in various fields. Introducing an impurity into semiconductor material can alter the material's properties, such as its conductivity, transparency, and charge mobility. ZnO has been doped by metallic such as Ni [6], Mn [7], Au [8], Al and Mg [9], and non-metallic elements, e.g., C [10], F [11], and S [12]. Sulfur has similar physical and chemical properties to oxygen. However, the bandgap energy of ZnS (~3.66 eV) is much higher than ZnO (~3.37 eV). Doping of S (sulfur) into ZnO has been reported to be able to influence the structure of the ZnO and increase light absorption [13] and improve the electrical and optical properties of ZnO [14].

In this research, pristine and S-doped ZnO nanorod thin film was prepared with various percentages of S (1% and 2.5%) via the seed-mediated hydrothermal method. The physical properties of S-ZnO samples were analyzed from the results of XRD characterization, FESEM, and UV-Vis spectrophotometer. The addition of sulfur into ZnO has improved the structural, morphological, and optical properties of ZnO nanorods.

METHOD

Chemical material

The chemicals used in this research, such as zinc acetate dihydrate $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, zinc nitrate hexahydrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, hexamethylenetetramine (HMT) $(\text{CH}_2)_6\text{N}_4$, sodium sulfide Na_2S , ethanol absolute $\text{C}_2\text{H}_5\text{OH}$, and deionized water ($\sim 18\Omega$).

ZnO and S-ZnO Thin Films Synthesis

The thin film of the S-ZnO nanorod was synthesized using the seed-mediated hydrothermal technique. This method consists of two steps, namely ZnO seeding and S-ZnO growth. The seeding stage begins with making a seeding solution, that is, dissolving zinc acetate dihydrate in absolute ethanol with a concentration of 10mM. The spin coating process was then carried out on the FTO substrate with a speed of 3000 rpm for 30 seconds. The sample was then heated using a hot plate at a temperature of 100°C for 15 minutes to produce ZnO seed. The growth solution was prepared by dissolving 5 mL of Zinc Nitrate Hexahydrate 50mM, 5 mL Hexamethylenetetramine 50mM, and 0.25 mL of Na_2S in DI Water. The ZnO seed was then immersed in a synthesis bottle containing the growth solution. The growth process was

proceeding at a temperature of 90°C for 5h. Finally, the sample was taken out and cleaned using DI Water. The physical properties of the S-ZnO sample were characterized using an X-ray diffractometer (7000 Shimadzu Diffractometer), Field Emission Scanning Electron Microscopy (FESEM, ZEISS MERLIN), and UV Vis spectrophotometer (HITACHI U-3900H).

RESULTS AND DISCUSSION

The crystal structure of the ZnO and S-ZnO thin films is known from the results of XRD characterization. FIGURE 1 shows the X-ray diffraction pattern from ZnO and S-ZnO samples. The XRD pattern results show diffraction peaks found at an angle of $2\theta = 34.43^\circ$; 36.26° ; 37.80° ; 47.54° and 51.62° . The matching results show the diffraction peaks of the hexagonal wurtzite ZnO crystal structure corresponding to the crystal plane (002), (101), and (102) based on data from Crystallography Open Database (COD) No. 96-210-7060. In addition to the ZnO phase, there is also an FTO crystal field symbolized by *. The diffraction peaks of the FTO are seen in pure ZnO samples and are further weakened by the addition of sulfur atoms to ZnO.

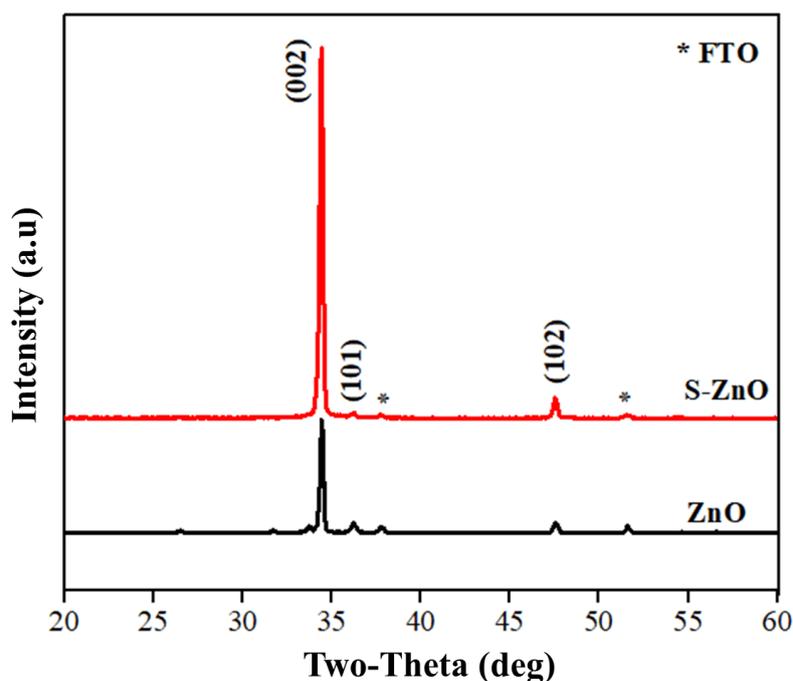


FIGURE 1. XRD Pattern of ZnO and S-ZnO Sample

The diffraction peaks of S-ZnO samples showed high intensity (sharp peaks) compared to pure ZnO samples, thus giving high crystalline properties. These results are following research conducted by Khan et al. [13]. The highest diffraction peak (strongest line) is in the crystal plane (002) which is in line with the study of Polsongkram et al ($a = b = 3,249 \text{ \AA}$ and $c = 5,264 \text{ \AA}$) [15]. This shows that the orientation of ZnO nanorod growth is in the direction of the c-axis, which is perpendicular to the surface of the FTO substrate. The ZnO and S-ZnO samples

crystallite sizes are 38.077 nm and 38.565 nm, respectively, which were calculated using the Scherrer equation.

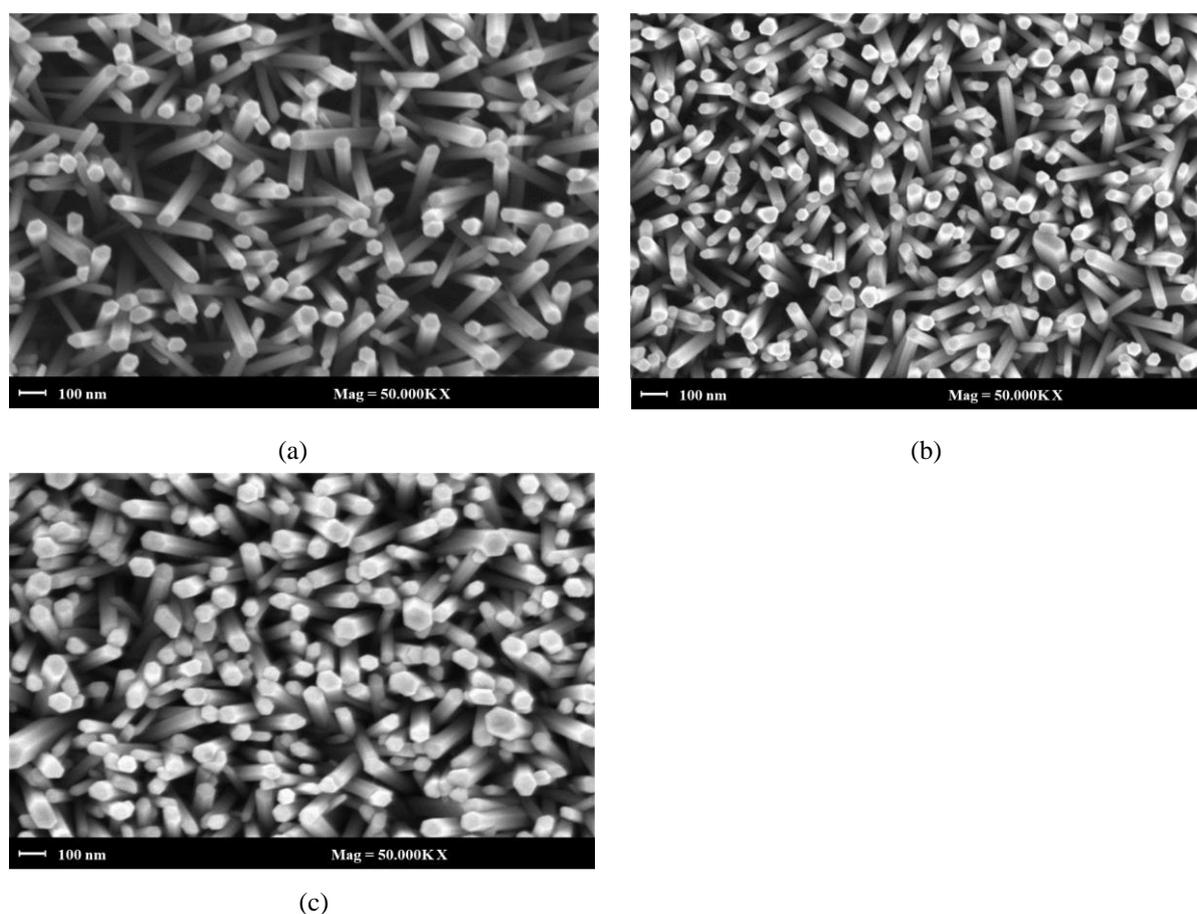


FIGURE 2. The Photo FESEM of (a) ZnO pure, (b) 1% S-ZnO and (c) S-ZnO 2.5%

FIGURE 2 shows the FESEM images of the resulting rodlike nanostructure as the concentration of sulfur increased. The geometric shape of the pure ZnO and S-ZnO samples are nanorods with a hexagonal cross-section. FIGURE 2a shows FESEM images of pure ZnO nanorods with a diameter of 42.1 ± 5.6 nm. In addition of 1% sulfur (1% S-ZnO), the nanorod diameter tends to decrease with a more uniform size distribution. As the concentration of sulfur increased up to 2.5% (2.5% S-ZnO) (FIGURE 2c), a larger diameter was observed with poor size distribution. It suggests that the small addition of S atoms to ZnO (1%-S) has changed the diameter and shape of nanorods. A similar result has been observed by Khan et al.

The optical properties of the ZnO and S-ZnO thin film samples can be known from the UV-Vis absorbance spectrum in FIGURE 3. The absorbance spectrum results show the optical absorption peaks occur in the wavelength range of 300-380 nm in the UV light spectrum. While in the visible light spectrum (380-800 nm), the optical absorption that occurs is weak. The optical absorption peak at a wavelength of 378 nm is in accordance with the ZnO nanorod reference [16]. Based on the UV-Vis absorbance spectrum, the absorption of S-ZnO samples increases with the addition of the S composition to ZnO. This increase in absorbance value

indicates the thickness of the sample, which increases with the addition of S atoms. The more non-transparent the sample shows that more ZnO molecules are produced so that the light absorbed will increase.

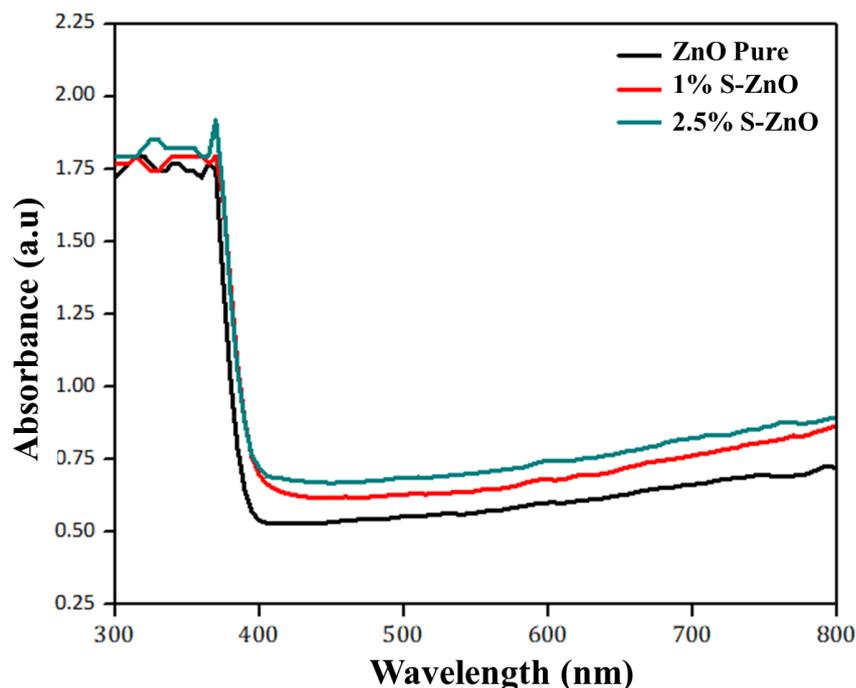


FIGURE 3. UV-Vis Absorbance Spectrum of Thin Film ZnO and S-ZnO

SUMMARY

Thin films of S-ZnO nanorod were successfully grown on FTO using the seed-mediated hydrothermal technique. XRD characterization shows that the addition of elemental sulfur can increase the crystalline size of ZnO from 38.077 nm to 38.565 nm. The morphology shown from the results of FESEM with the addition of sulfur atoms gives a higher density of nanorod growth, especially in the 1% S-ZnO sample. The results of UV-Vis absorbance spectra showed that the absorption peak had increased at sample 2.5% S-ZnO. Based on the crystal structure, morphology, and the level of UV-Vis absorbance from the results of this research, S-doped ZnO can improve the physical properties of ZnO so that it can potentially be applied in the fields of photocatalysts, gas sensors, and solar cells.

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