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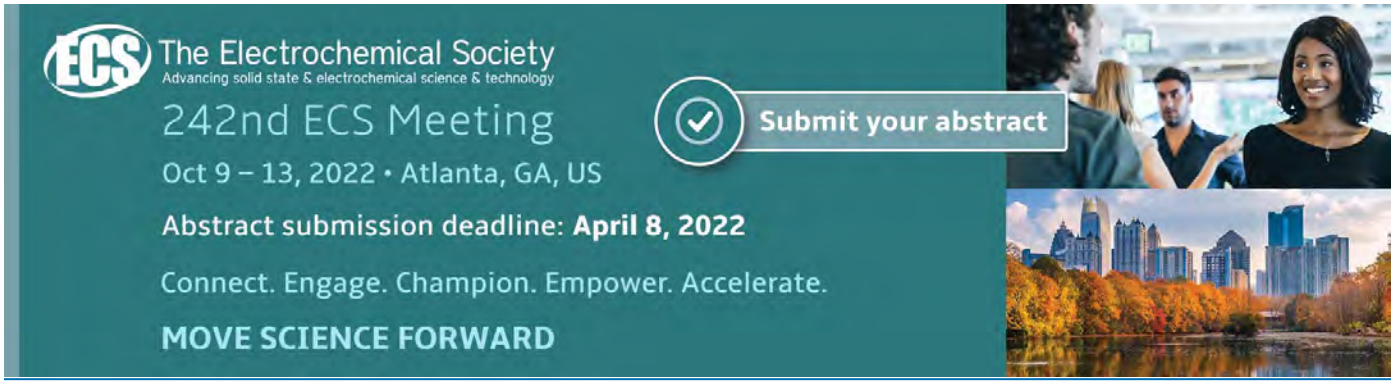


Synthesis and optical properties of Sb-doped ZnO thin film by sol-gel spin coating method

Nurdin Siregar[1*], Makmur Sirait[1] and Motlan[1]
[1]Department of Physics, Faculty of Mathematics and Natural Sciences, State University of Medan, Jl. Willem Iskandar Pasar Medan Estate, Medan 20221, Indonesia

*Email : siregarnurdin@unimed.ac.id

Abstract. Sb-doped ZnO thin films had been successfully synthesized by the sol-gel spin coating method. The results of XRD analysis of ZnO and Sb-ZnO thin films showed a hexagonal wurtize crystal structure with crystal sizes of 21,251 nm and 11.265 nm, respectively. The results of SEM analysis showed that the grain size distribution of the crystallites was round and uniform, compactly covering the substrate and almost no porosity. The percentage of Sb concentration based on EDS analysis was 3.02%. UV-Vis analysis results showed the absorbance and transmittance values of Sb-ZnO thin films were higher than the transmittance values of ZnO thin films. The energy band gaps for ZnO and ZnO:Sb thin films were 3.20 eV and 3.30 eV, respectively.

1. Introduction

In material engineering, especially thin films, ZnO is an attractive material for use in sensors, solar cells, and nanodevices, due to its emission properties near to UV light, high conductivity and transparency, and as a photocatalyst [1] and have properties good optical, electrical and piezoelectric properties [2]. ZnO is one of the basic materials for making thin films because it has a wide energy band gap of 3.37 eV and an excitation binding energy of 60 meV at room temperature [3]. The disadvantages of ZnO thin films are that they have poor electrical characteristics, namely the low conductivity value of 6.24×10^{-7} $(\Omega cm)^{-1}$ [4]. To improve the physical, optical and electrical properties of ZnO often doped with extrinsic dopants, using various types of materials such as B, Al, and Ga as foreign bodies which are substituted into the ZnO structure [5-6]. Antimony (Sb) material was chosen as doping because it can replace O and Zn ions [7]

Multiple synthesis methods Thin film slike molecular beam epitaxy [8], RF Sputtered [9], *spray pyrolysis* [10], *pulse laser deposition* [11], Molecular Beam Epitaxy [12] and sol-gel [13]). The sol-gel spin coating method is used because the synthesis temperature is low and the equipment is simple and inexpensive.does not use a space with a high vacuum, they composition is homogeneous, the layer thickness can be controlled and the microstructure is quite good [14].

Many studies have been carried out on ZnO doped Sb (Antimony) thin films, among others by [15] with variations in the concentration of Sb (0,1, 2, and 3%), the result is that the energy band gap value decreases with increasing doping concentration. according to [16], with variation of Sb doping (1, 3, 5%), the result is transmittance >80%. The higher the Sb doping concentration, the smaller the transmittance of the energy band gap.According to [17] with the doping concentration (0; 0.2 and 0.4),

the result is ZnO without doping type n and with doping type p, the lowest type of inhibition at 0.2% doping and the highest concentration of charge carriers without doping.

2. Experiment

The materials used in this research were Zinc Acetate Dehydrate, antimony chloride, isopropanol and diethanolamine (DEA) as base material, doping material, solvent and stabilizer, respectively. Gel synthesis was carried out using the sol-gel spin coating method. Zinc acetate dehydrate and antimony chloride were dissolved in 50 ml of isopropanol as shown in Table 1. The solution was then stirred with a magnetic stirrer for 30 minutes, and 2 ml of diethanolamine (DEA) was added drop by drop, and heated at 60ºC for 2 hours. Then cooled to room temperature so that the solution or gel looked clear and transparent. The coating wad done by dripping the solution/gel on the FTO glass substrate and rotated with a spin coating speed of 5000 rpm, then heated at a temperature of 100ºC and held for 3-5 minutes. Coating was repeated three times. The sample was then annealed at 500ºC for 5 hours and held for 10 minutes. The samples were then characterized by XRD, SEM, EDX and UV-Vis.

Table 1. Comparison Zinc Acetate Dehydrate and Antimony Chloride

Sample	Zinc acetate dihydrate	Antimony chloride
ZnO	5.0 gr	0 gr
Sb-ZnO	4.75 gr	0.25 gr

3. Results and Discussions

3.1. Crystal Structure of ZnO and Sb-ZnO

The XRD diffraction pattern of the ZnO and Sb-ZnO thin film samples is shown in Figure 1. The results of the XRD diffraction pattern analysis for the sample without doping and with doping have the same crystal planes, namely (100), (002) and (101), and the same growth peak and are field-oriented (101). The c/a ratio for all samples has the same value as the ideal value for hexagonal cells c/a = 1.602 [18]. These results indicate that the crystals are hexagonal wurtzite and match the standard ZnO data of the JCPDS 80-0075 card. These results also showed that Sb doping did not change the crystal structure.

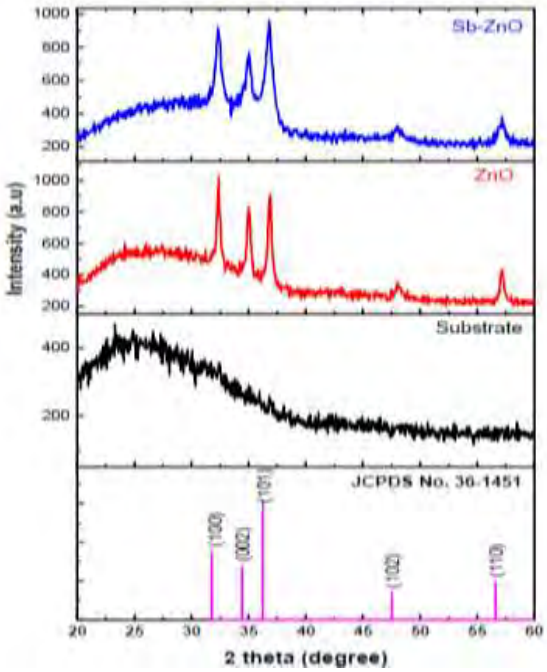


Figure 1. XRD Spectrum of Samples and Substrate

The crystal sizes of ZnO and Sb-ZnO obtained in Table 2 using the Scherrer equation [19] are:

$$D = \frac{0{,}9\,\lambda}{\beta \cos\theta} \quad (1)$$

with D = crystal size, λ = wavelength, β = FWHM (full width half maximum), θ = diffraction angle.

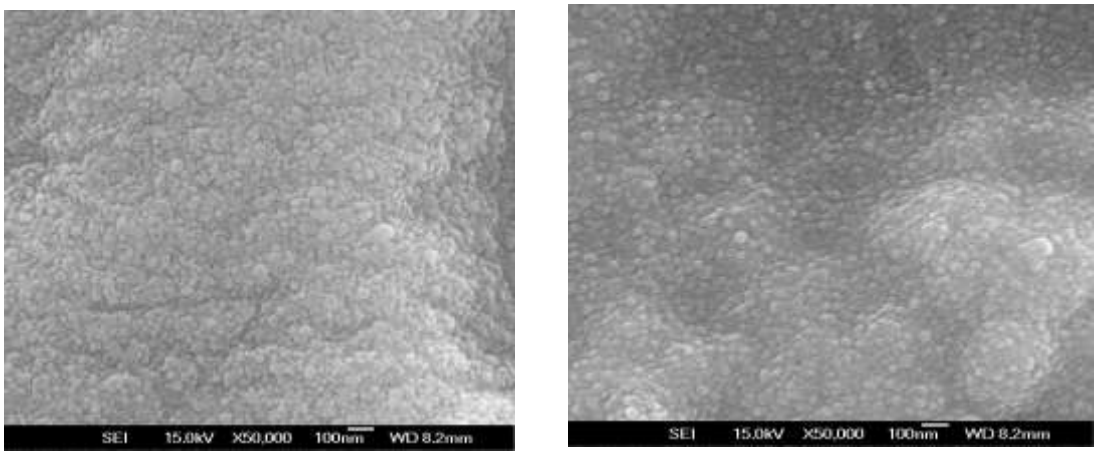
Table 2. Sample Crystal Size

Sample	Phase	Peak		Crystal Size (nm)
		2θ (degree)	FWHM(rad)	
ZnO	ZnO	36.8930	0.0068753	21.251
Sb-ZnO	Sb-ZnO	36.7930	0.0129653	11.265

The crystal size obtained is getting smaller with the presence of Sb doping, this is in accordance with the results of the study [20]. This result can be explained by the introduction of Sb into ZnO cells, which causes Sb to combine with ZnO thereby increasing stress and causing ZnO crystals to break, resulting in smaller crystallite sizes. Therefore, the small crystal size can cause quantum dot regimes and Blue Shift events due to Sb doping and is largely ascribed to the Burstein-Moss effect, i.e. the increasing value of the optical band gap energy Eg in Sb-ZnO.

3.2. Morphology of ZnO and Sb-ZnO Thin Film

The growth process of ZnO and Sb-ZnO thin films was observed through morphological recordings using a scanning Electron Microscope (SEM) whose results are shown in Figure 2. The results obtained showed that the surface morphology of the ZnO thin films was less uniform and consists of larger grains, while the surface of Sb-doped ZnO thin film showed a relatively more even surface and no porosity and amperage, and the distribution of crystallite grains with smaller sizes was uniform and compact. The atoms in the smaller grains get enough driving force to diffuse to form new larger grains.

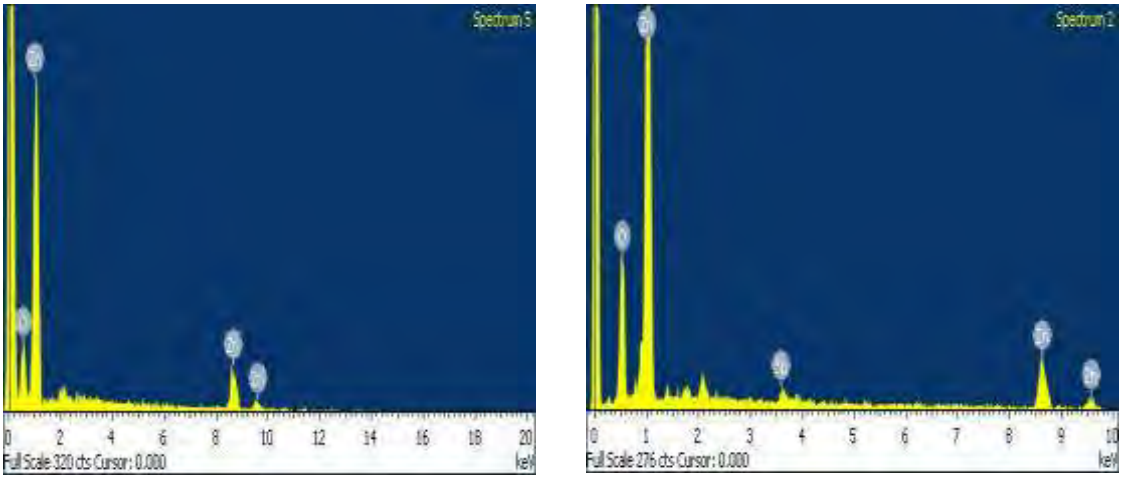


(a) (b)

Figure 2. SEM photo of the surface: a. ZnO Thin Film. b. Sb-ZnO Thin Film

3.3. Elemental Content in Sample

To find out the elements contained in the sample and the distribution of elements (mapping) in the sample, the EDS test was carried out, the results of which are shown in Figure 3 and Table 3.



(a) **(b)**

Figure 3. Distribution of Elements: a. ZnO. b, Sb-ZnO

Based on Figure 3, the percentage of atoms contained in the sample is shown in Table 3.

Table 3. Atomic Percentage of ZnO and Sb-ZnO

Sample	Sb	Zn	O
ZnO	-	48.23	51.77
Sb-ZnO	1.38	44.28	54.35

EDS measurements revealed the presence of Zn (44.28%), oxygen (54.35%) and antimony elements (1.38%) in the ZnO:Sb thin film. These results show the percentage of Sb concentration based on EDS analysis was 3.02%. Based on the results of the EDS showed that there was incorporation of Sb into the ZnO main, this was in accordance with XRD analysis. The absence of other elements associated with impurities confirms the pure phase of the Sb-doped ZnO film. In addition, the lack of Zn (44.283%)

compared to O (54.35%) in principle can indicate the presence of density which is very important in filling the Zn vacancies in the lattice.

3.4. Optical Properties of ZnO Thin Film and Sb-doped ZnO Thin Film

Transmittance and absorbance spectra for all samples of UV-Vis test results in the range of 300-500 nm to analyze the absorbance and transmittance shown in Figure 4

(a) (b)

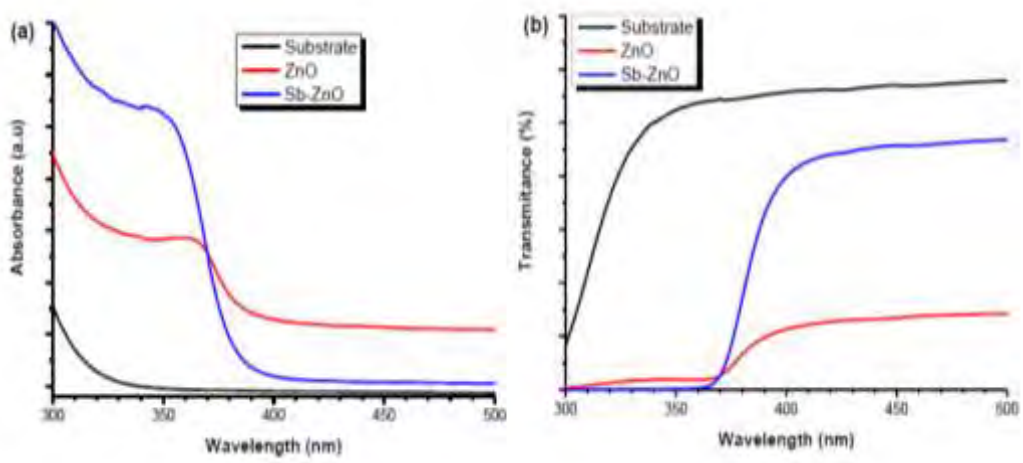


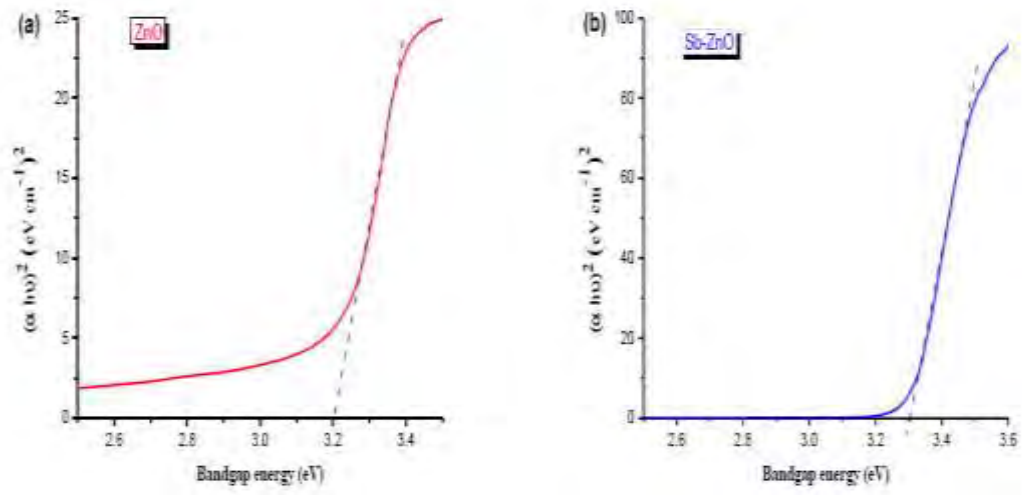
Figure 4. a. Absorbance Spectrum. b. Transmittance Spectrum

Based on Figure 4.a, it can be seen that the absorbance value of the Sb-ZnO thin film is higher than the absorbance value of the ZnO thin film and in all samples there is a sharp decrease in the absorbance value that occurs in the wavelength range of approximately 350-400 nm which is the region ultraviolet wavelengths and Sb doping cause shifts the absorption edge towards the region of lower wavelength. The transmittance spectrum of all samples in Figure 4.b showed a fairly sharp increase in transmittance value in the wavelength range of approximately 350 – <400 nm and an increase in transmittance value along with the presence of Sb doping. The high transmittance value of Sb-ZnO thin films can be applied to solar cells. According to [21], high transmittance values of thin films can be applied to solar cells. According to [22] thin films that have high transmittance in the visible light region, can be used as transparent window materials in optoelectronic devices

For materials with a direct band gap, the relationship between the absorbance and the photon frequency satisfies Eq [23] are:

$$(\alpha hv)^2 = C_D(hv - E_{opt}) \quad (2)$$

Based on the Tauc Plot method, the energy band gap of the ZnO and Sb-doped ZnO thin film were obtained as shown in Figure 5.



(a) **(b)**

Figure 5. a. Band gap of ZnO. b. Band gap of Sb-ZnO using Tauc Plot method

Based on Figure 5, the energy gap width of ZnO and Sb-ZnO thin films is obtained as shown in Table 4.

Table 4. Sample energy band gap

Sample	**Bandgap (eV)**
ZnO	3.20
Sb-ZnO	3.30

Sb doping causes a change in the energy band gap value of 0.1 eV, this is in accordance with research [20]. The energy band gap of Sb-ZnO is larger than that of ZnO, this is because Sb doping facilitates widening of the energy band gap in the ultraviolet region.The Blue Shift event on Sb doping is mostly ascribed to the Burstein-Moss effect, namely the increasing value of the optical band gap energy Eg on Sb-ZnO thin films and is in accordance with research [24,25] which states that doping can increase the value of the energy band gap.

4. Conclusion

Sb-doped ZnO thin films have been successfully synthesized by the sol-gel spin coating method. Crystal size of Sb-ZnO is smaller than ZnO crystal size. The percentage of Sb concentration based on EDS analysis was 3.02%. The absorbance and transmittance values of Sb-ZnO thin film is higher than the absorbance values of ZnO thin film due to doping Sb. After being doped with Sb, the bandgap energy increased by 0.1 eV compared to pure ZnO without doping.

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