Effect of Deposition Current on Optical Properties of ZnO Thin Film Using Electroplating Method

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Abstract. ZnO thin films with various deposition currents have been successfully fabricated by the electroplating method. The X-ray diffraction analysis showed that ZnO thin film with variations of deposition currents had a hexagonal crystal structure and crystallite sizes of 21.14 to 29.69 nm. The morphological analysis show that the deposition current increases as the grains that are formed are almost uniformly compact and cover the substrate, and the porosity is getting smaller. The results of UV-Vis spectrophotometer reveal that the transmittance value of ZnO thin films for all samples was above 80%. Bandgap values of ZnO thin films range from 3.15 to 3.24 eV.

Keywords: ZnO thin film, deposition current, electroplating method

1 Introduction

ZnO as an n-type semiconductor that has a bandgap and binding energy of 3.37 eV and 60 meV, respectively, at room temperature [1, 2]. In addition, ZnO has multi-functional properties with high energy binding strength, low resistivity, and great light-trapping properties, making it one of the most promising thin film materials for various applications [3, 4]. Thin film synthesis methods include pulsed laser deposition, physical vapor deposition, molecular beam epitaxy, spray pyrolysis, and RF sputtered [5–9].

To obtain the most optimal ZnO thin film fabricated by the electroplating method with variations in the deposition current, because the above method has several drawbacks, such as expensive equipment costs. The advantages of the electroplating method include the low synthesis temperature and simple and cheap equipment, without use of vacuum chamber, the composition is homogeneous, the layer thickness can be cotrollble, and great microstructure, allowing to be widely used as an alternative in making thin films [10, 11].

Several studies on thin films with the electroplanting method, among others, have been carried out [12] By varying the deposition potential, the result is the highest transmittance of 80% at a potential of -1.7 V, the energy band gap decreasing as the potential increases, and the lowest resistivity at a potential of -2.1 V. According to [13] with variations in $ZnFe_2O_4$ concentration, the results bandgap energy lowered with higher concentration of ZnFe2O4. According to [14], with potential variations, the results show that the potential difference at electrodeposition has an influence on the coating process and the morphology of ZnO; the higher the potential used

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at electrodeposition, the lower the resistance value, and the best coating occurs at a potential of -1.0 V. According to [14] [15] with the variation of the deposition current, the result is that the crystallite size and bandgap elevates value as the deposition current increases.

2 Experiment

The materials used in ZnO thin film fabrication are $ZnSO_4$ powder, Di water, zinc metal, and ITO glass as substrates for ZnO thin film electroplating. Prior to the coating process, the ITO glass was cleaned with an ultrasonic cleaner in acetone and ethanol for 5 minutes each. To obtain the desired concentration of solution, a certain amount of $ZnSO_4$ powder was added into 50 mL of destiled water and ultrasonically stirred for 15 minutes until the solution appears uniform. Electroplating was performed with a two-electrode uding ITO glass as the working electrode (negative) and zinc metal as the reference electrode (positive) placed parallel to each other at a distance of about 2 cm. Fabrication of ZnO thin film samples was carried out by the electroplating method using a potentiostat with a solution concentration of 0.2 M; deposition time of 2.50 minutes, and variations in deposition currents of 5, 10, 20, and 40 mA. After electroplating, the samples were heated to 100 °C for 30 minutes, and heating was carried out in a furnace with a temperature of 500 °C and held for 15 minutes with a heating time of 2 hours, resulting in the formation of ZnO thin film samples, which aim to remove solvents, water, and acid groups, and facilitate the formation of ZnO samples. The as-prepared ZnO samples were further analyzed.

3 Results and Discussion

3.1. Crystal properties

X-ray diffraction pattern of the samples with variations in deposition currents (5, 10, 20, and 40 mA) are presented in Figure 1. The results reveal that all samples have the same peaks with (100), (002), and (101) planes, showing the same growth peak. The ideal value of lattice parameters *c/a* ratio for hexagonal cells is 1.602 [16]. This demonstrates that the crystal structure is hexagonal and in accordance with ZnO standard data on JCPDS card No. 36-1451. These results also show that the deposition current does not change the crystal structure.

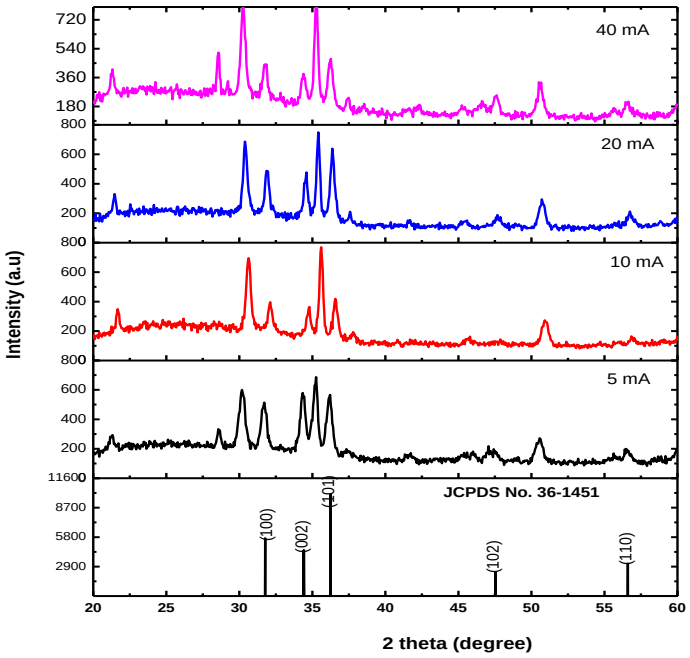

Figure 1. XRD pattern of ZnO Samples with Variation of Deposition Current

The crystallite sizes ZnO thin film with variations in deposition currents (5, 10, 20, and 40 mA) were estimated using Scherrer formula and the results are listed in Table 1 [17]:

$$d = \frac{0.9\,\lambda}{\beta \cos\theta} \quad (1)$$

Table 1. Crystal properties of Sample with Variation of Deposition Current

Sample	Phase	Peak		Crystal Size (nm)
		2θ (degree)	FWHM(rad)	
5 mA	ZnO	31.69	0.434	21.14
10 mA	ZnO	32.11	0.326	28,17
20 mA	ZnO	31.89	0.309	29.69
40 mA	ZnO	31.77	0.316	29.05

Crystallite size depends on the value of Full Width Half Maximum (FWHM) of a peak. If the FWHM value is small then the crystal size is large, and vice versa. Based on Table 1, it can be seen that the crystal size increases with increasing deposition current up to 20 mA. The increase in deposition current is in line with the increasing number of constituent atoms in the ZnO thin film crystal growth process, so that the crystal size increases. Furthermore, the crystal size began to decrease when the deposition current was increased to 40 mA. The greatest crystallite size is 29.61 nm using a deposition current of 20 mA. According to [18], by varying the current, the result is that the crystallite size and bandgap energy lower as the deposition current increases.

3.2. ZnO Thin Film Morphology

The morphology of ZnO thin films with variations in deposition currents was analyzed using SEM, the results of which are shown in Figure 2. The results obtained show an increase in deposition currents as the grains that form almost uniformly and compactly cover the substrate and the porosity becomes smaller. This is because there are smaller grains that have enough energy to diffuse and form new, larger grains. Deu to this diffusion between grains, a necking will form, which results in a smaller boundary between grains

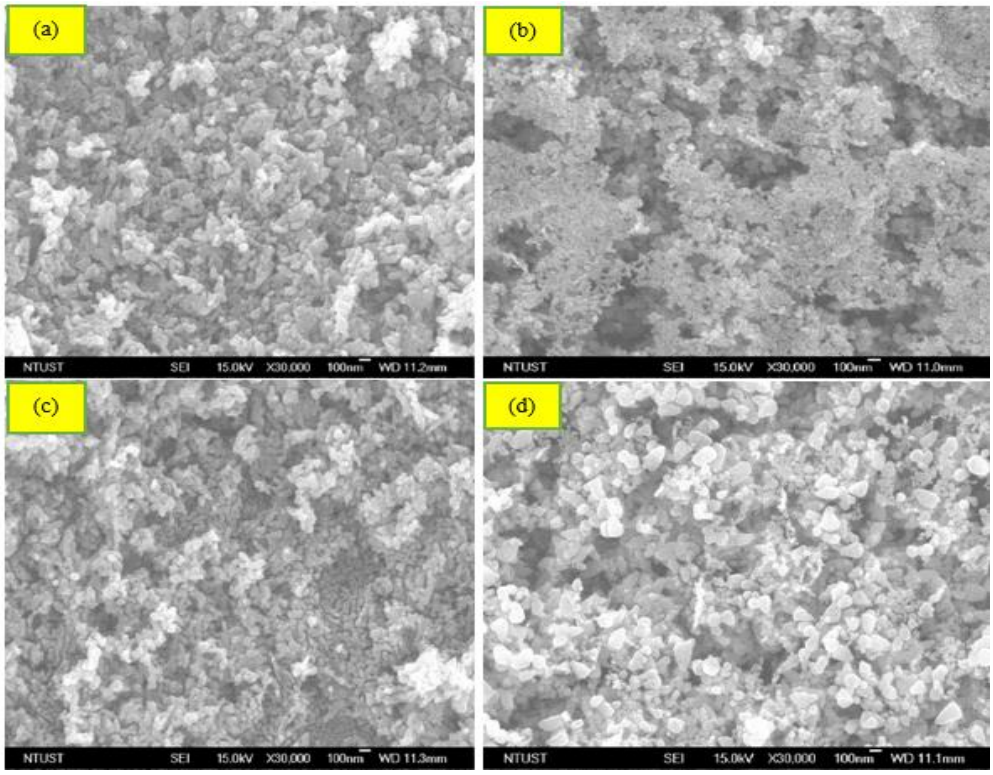

Figure 2. SEM images of the top surface ZnO Thin Film sample with Deposition : (a) 5 mA, (b) 10 mA, (c) 20 mA, and (d) 40 mA

3.3. Elemental Composition

To find out the elements and the composition for various deposition currents, analysis was carried out with EDS. Figure 3 shows the EDS spectrum of ZnO thin films at various deposition currents with Zn and O peaks very clearly visible throughout the EDS spectrum.

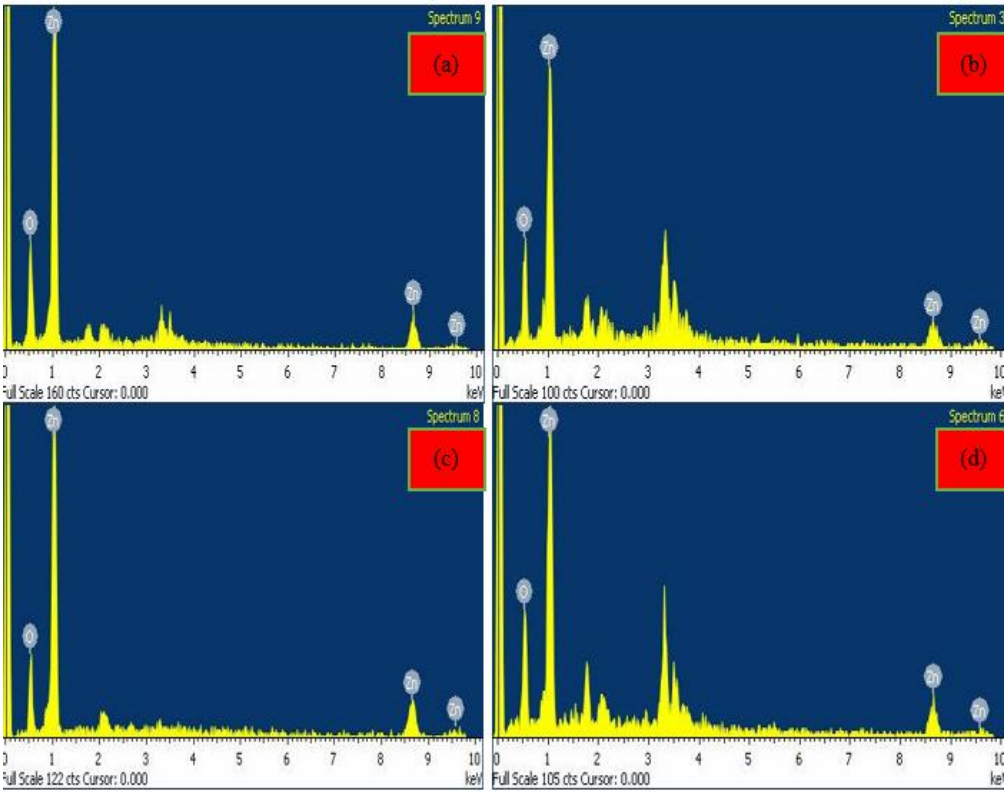

Figure 3. Composition of ZnO Thin Film Elements with Variation of Deposition Current: (a) 5 mA, (b) 10 mA, (c) 20 mA, and (d) 40 mA

According to Figure 3, the atomic percentage of Zn and O in the sample is shown in Table 2

Table 2. Zn and O percentages of ZnO Thin Film Elements with Variation of Deposition Current

Sample	Zn (%)	O(%)
5 mA	44.58	55.42
10 mA	41.43	58.47
20 mA	50.42	49. 58
40 mA	38.18	61.82

EDS measurements for samples with variations in deposition currents of 5, 10, 20, and 40 mA indicated that the highest percentage of Zn contained in the ZnO thin film was 53.33% at 10 mA current strength and as low as 38.18% at 40 mA current strength. The highest percentage

of O is 61.82% at a deposition current of 40 mA, and the lowest is 46.67% at a current of 10 mA.

3.4. ZnO Thin Film Optical Properties

To evaluate the optical properties of ZnO thin films with different deposition currents, the transmittance and absorbance spectra were tested with a UV-Vis spectrophotometer in the range of 200–600 nm. Figure 4a shows a sharp decrease of absorption values that occurred at wavelength of 300–400 nm, which is UV range and an increase in solution concentration caused a shift in the absorption edge towards shorter wavelengths. The transmittance spectra in Figure 4b show a sharp increase in the transmittion values at a wavelength of around 300–450 nm. The increase in deposition current is in line with the decrease in the transmittance value and the increase in the absorbance value. This is because the more the deposition current increases, the more constituent atoms lead to more collision between the light and particles, making the light diffult to pass through. Transmittance values for all ZnO thin film samples are > 80% so that they can be applied to solar cells. The great transmittion value of this thin films allows them to be used as a DSSC photoanode [19].

To further investigate the optical properties of ZnO thin films, photoluminescence spectroscopic analysis was performed at an excitation wavelength of 250 nm. The emission is then recorded at a wavelength of 300–700 nm. As demonstrated in Figure 4c, the emission characteristics of all ZnO thin films at different deposition currents are the same at peak emission but have different intensities. The highest peak emission is located at a wavelength of about 400 nm, which corresponds to the UV emission and the band gap of ZnO. The second peak at 480 nm corresponds to the presence of oxygen vacancies. The sharpest intensity gradually decreased when the deposition current was increased from 5 mA to 40 mA, indicating a lower electron-hole recombination. [20]

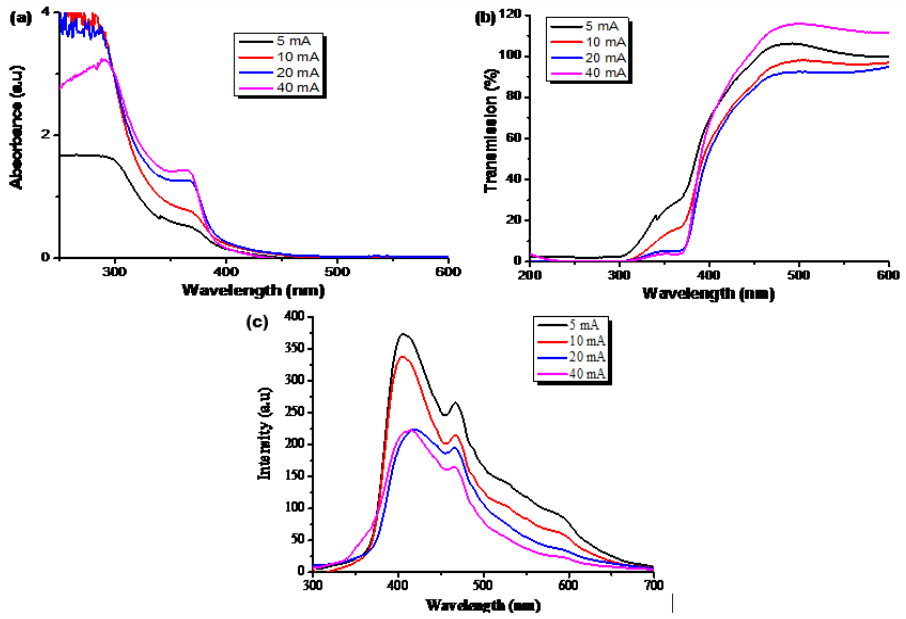

Figure 4. Optical Properties of ZnO Thin Films with Variation of Deposition Current: (a) absorption, (b) transmission and (c) photoluminescence spectrum

The relationship between absorbtion and photon energy for materials with a direct band gap is given by the equation below [21]:

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

As shown in Figure 5, the band gap energy of ZnO thin films with varying concentrations of deposition currents was determined using the Tauc Plot method.

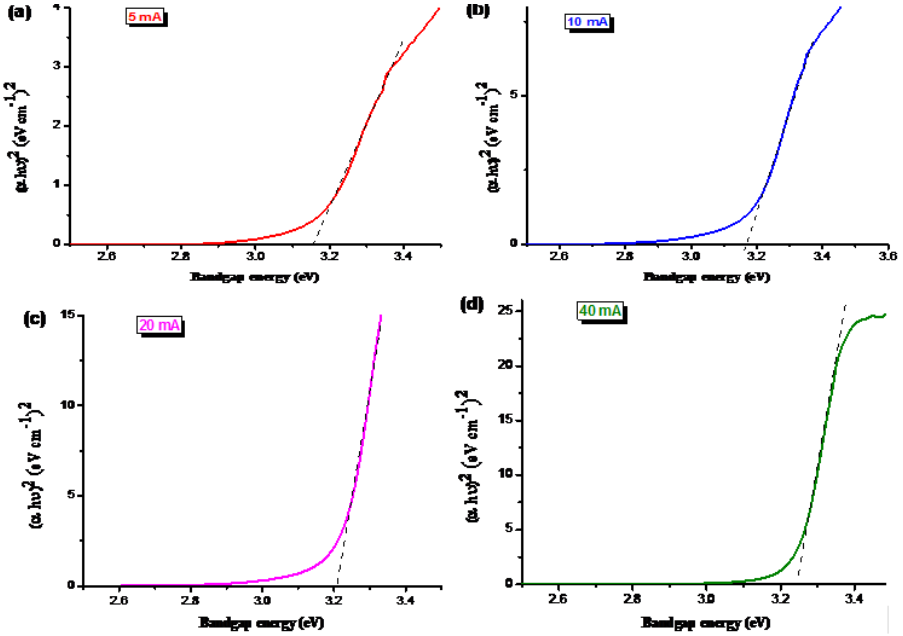

Figure 5. ZnO Thin Film Energy Band Gap Variation of Deposition Current: (a) 5 mA, (b) 10 mA, (c) 20 mA, and (d) 40 mA

Based on Figure 5, the energy gap width of the ZnO thin film for the deposition current samples of 5, 10, 20, and 40 mA is obtained as shown in Table 3.

Table 3. Bandgap energy value of samples

Sample	Bandgap (eV)
5 mA	3.15
10 mA	3.17
20 mA	3.21
40 mA	3.24

Based on Table 3, it can be seen that the deposition current increases with increasing energy band gaps. Several factors affect the value of the energy band gap, such as the uneven surface of the ZnO thin film, which can cause light reflection at different angles so that it appears as if there is absorption at visible wavelengths and can also be caused by blue-shift events. Most of

the Blue Shift events can be explained with Burstein-Moss effect, which is an increase in the bandgap energy value of ZnO thin films as the deposition current increases. According to [22], the value increases with increasing deposition current.

4 Conclusion

ZnO thin films with various deposition currents have been successfully fabricated by the electroplating method. The largest ZnO thin film crystal size is 29.61 nm at a deposition current of 20 mA. The more the deposition current increases, the more visible the grains that almost uniformly and compactly cover the substrate, and the smaller the porosity becomes. The deposition current affects the percentage of Zn and O contained in ZnO. UV-Vis analysis indicated that the transmittance value of ZnO thin films was greater than 80% for all deposition current samples. The greatest bandgap energy value of sample was 3.24 eV at a deposition current of 40 mA.

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