SPEKTRA: Jurnal Fisika dan Aplikasinya
Volume 7, Issue 1, April 2022
Homepage: doi.org/10.21009/SPEKTRA

DOI: doi.org/10.21009/SPEKTRA.071.04

THE EFFECT OF VARIATION CONCENTRATION AND DEPOSITION PARAMETER TO THE OPTICAL CHARACTERISTICS AND THE CRYSTALLITE PROPERTIES OF ZINC OXIDE

Waode Sukmawati Arsyad*, Ulpiani, Muh. Angga Anugerah, La Aba, Ida Usman

Department of Physics, Faculty of Mathematics and Natural Sciences, Halu Oleo University, Kendari, South East Sulawesi, Indonesia

*Corresponding Author Email: wdsukmawati@uho.ac.id

Received: 25 August 2021
Revised: 2 March 2022
Accepted: 29 April 2022
Online: 30 April 2022
Published: 30 April 2022

SPEKTRA: Jurnal Fisika dan Aplikasinya
p-ISSN: 2541-3384
e-ISSN: 2541-3392

ABSTRACT

The objective of the study was to obtain the ZnO thin films with variation concentration of zinc acetate dehydrate (ZAD), and variation of spin coater speed and rotation time. We observed the effect of the former parameters on the optical characteristics that comprised of the spectrum of absorption, transmittance, and ZnO crystallite size from UV-Vis spectrometer and XRD orderly. For the analysis of the effect of the variation of concentration, ZAD diluted into ethanol with the concentration 0.1M, 0.25M, 0.5M, 0.75M and 1M, with the addition of diethanolamine (DEA). Then it was deposited on the glass substrate with spin coater, continued by the heating on the hotplate with the number of layer's variation. For the analysis of deposition parameter effect on the transmittance and the size of ZnO crystal, we used 0.25M ZnO precursor solution with the addition of DEA, then deposited by speed and time of rotation of spin coater of 1230 rpm, 2500 rpm, and 3200 rpm for 10, 15 and 30 seconds of each. The smallest absorbance value 0.05 obtained for single layer 0.1M ZnO, while the maximum transmittance value obtained for three-layer 0.25M ZnO. Concentration variation did not affect the energy gap, whose value was approximately 3.2 eV for all samples. From the XRD result, we found that deposition time affected the number of diffraction lines, the size of the crystallite, and the transmittance.

Keywords: zinc oxide, crystallite properties, deposition parameter

INTRODUCTION

The ZnO has been widely used to handle various things such as pharmaceutical waste [1], printing waste, and paper wastewater, the catalytic activity of ZnO is much better than other materials because ZnO can absorb light in a broader spectrum than other materials [2]. The optical properties of semiconductor materials are related to the intrinsic and extrinsic effects of these materials. Electrons play intrinsic optical transition in the conduction band and holes in the valence band, including the excitonic effects originating from the Coulomb interaction. Extrinsic optical transition is related to dopants or disabilities, which can produce a new level of energy around the bandgap. The emergence of this new energy level can affect the optical properties of the adsorption and emission processes. The electronic state of the attached excitons depends on the band structure of the semiconductor material in question. In theory, excitons can be attached to neutral or charged donors and acceptors.

As a transparent material and electricity conductor, a thin layer of ZnO is suitable to be applied to the active components of solar cells. The role of the ZnO-containing layer in this device is the acceptor layer that accepts electrons and delivers them to the cathode. As a material with a large enough bandwidth and includes a direct energy gap (direct bandgap), this material is very suitable for use in electronic and optoelectronic devices. The advantages associated with energy gap widths in this material are higher breakdown stress, the ability to withstand or continue the presence of large magnetic fields, produce less noise, and use of materials based on this material can be carried out at high temperatures and power.

The characteristics of ZnO crystals depend on their size and method of preparation. ZnO crystal preparation with nano-size has been carried out by different methods such as micro emulsions [3], precipitation method [4], hydrothermal [5], chemical vapor deposition [6], solid-state reaction, wet chemical synthesis, spray pyrolysis method [7]a nd sol-gel method [8]-[9]. Therefore, the development of ZnO nanocrystal synthesis using a simple and economical method is now significant. In previous studies, ZnO nanocrystals have been made from zinc acetate precursors with oxalic acid with water, methanol, and ethylene glycol as a solvent [10].

The method of making sol-gel is a precursor or starting material in its manufacture is metal alkoxide and metal chloride, which then undergoes a hydrolysis reaction and a polycondensation reaction to form a colloid, which is a system consisting of solid particles (particle size between 1 nm to 1 μm) dispersed in a solvent. Making thin films by the sol-gel method has several advantages, including low cost, not using space with high vacuum, homogeneous composition, the thickness of the layer can be controlled, and the microstructure is quite good [11].

Thin layer deposition techniques divided into four classes, namely atomic growth [12], particulate deposition [13], bulk coating (dip coating [14], spin coating [15]), and surface modification. Of the several thin layer deposition methods, the spin coating deposition method is the easiest, cheapest, and most straightforward. Spin coating is a method of depositing a thin film on a substrate by dripping liquid to the center of the substrate that rotated at a constant high speed. The spin coating method is a combination of physical and chemical methods used to make polymeric and semiconductor materials on substrates such as glass or silicon. Synthesis of thin films by the sol-gel spin coating method is widely used because the method is straightforward, practical, and uncomplicated by adjusting the time parameters, rotation speed, and thickness of the gel or solution. This method also has several advantages such as relatively low cost, no need to use a vacuum chamber, the composition obtained has high homogeneity, the thickness of the layer can be controlled, and the microstructure is very good, so this method is widely used in the thin film industry.

One material that can be created by using spin coating deposition is ZnO. The ZnO is a semiconductor material that commonly applied to optoelectronic devices. This material has electrical, optoelectronic, and photochemical properties that have been widely used in solar cell devices, transparent electrodes, and Light Emitting Diodes (LEDs). ZnO is known as an alternative material for TiO_2 as a semiconductor electrode, where the use of ZnO can improve the efficiency of the current collection. ZnO in the form of nanocrystals provides a large internal surface area for attachment of dye molecules and also provides a percolation pathway for electrons.

METHOD

Thin Film Preparation

Making ZnO with the sol-gel method was based on the work done by [16] redescribed in [17]. ZnO precursors are derived from zinc acetate dehydrate (ZAD) with concentrations of 0.1M, 0.25M, 0.5M, 0.75M, and 1M in 5 ml of ethanol. Stirred using a stirrer bar for approximately 5 minutes, after the solution mixed, then diethanolamine (DEA) is added. After a few moments, the precursor solution will look bright and colorless. This solution was then ready to be deposited on a rectangular glass substrate with a size of 1.5 x 2 cm, which was first cleaned with teepol and alcohol while vibrated with an ultrasonic cleaner for 5 minutes to remove oil and dirt content attached to the substrate. After the precursor solution dropped on the substrate, the substrate rotated with a rotational speed of 2500 rpm for 30 seconds. The heating process carried out using a hot plate with the temperature gradually increasing, starting at a temperature of 100^oC, 290^oC and 500^oC for 10, 30, and 30 minutes respectively. The same method used for the second to the fifth coating process.

To investigate the effect of deposition parameters on optical properties and crystallite size, we used a precursor with a concentration of 0.25 M, where the ZnO precursor solution deposited on a glass substrate by varying the speed and rotational time of 1230rpm, 2500rpm and 3200rpm for 10 - 30 seconds, to obtain the best, flat, and homogeneous coating.

Characterization

Optical properties of thin films, which include absorbance and transmittance measured using UV-Vis Spectrophotometer Ocean Optics 2000, from the absorbance spectrum results, we estimated the energy gap value (Eg) of the resulting ZnO thin film. Characterization of crystal structures using X-Ray Diffraction (XRD), and from the XRD results an estimation of the size of the crystallite calculated using the Scherer formulation:

$$D = \frac{k\lambda}{\beta cos\theta} \tag{1}$$

where k is the Scherrer constant (0.94 for spherical crystals), λ is the X-ray wavelength used, and β is the peak width (FWHM), which obtained from spectral matching.

RESULT AND DISCUSSION

Effect of variations in concentration on optical properties

Absorbance spectrum

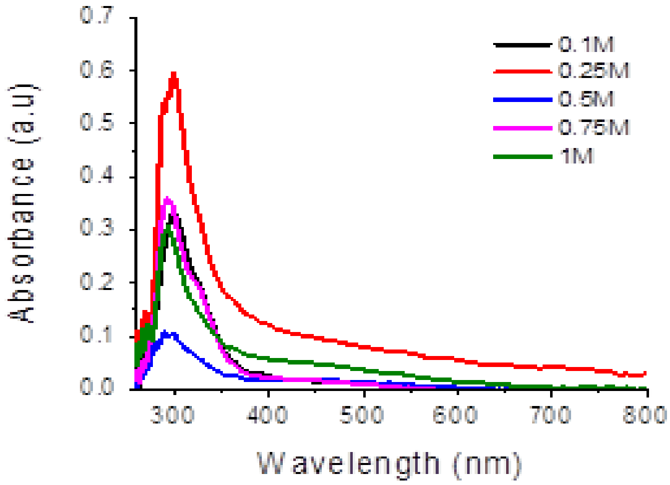
FIGURE 1 (a) and (b) shows the measurement results of the absorbance spectrum of the ZnO precursor solution and one layer of the thin film. Compared with the precursor solution, which has a broader absorption area where the absorption edge is at a wavelength of 700nm with the absorption peak at a wavelength of 300nm, on ZnO thin films, the absorption area starts at wavelengths of 300 to 400 nm with absorption peaks shifted at 340nm wavelength region. The narrowing of the absorption area is related to the loss of absorption contribution by solvents and other additives due to the heating process.

For all concentrations, the absorption area is in the range of 300nm - 700nm with the absorption peak at a wavelength of ~300nm (FIGURE 1(a)) where the difference only appears in the absorbance intensity for each concentration of the precursor solution. The absorbance value initially increases from concentrations of 0.1M to 0.25M, and then decreases at a concentration of 0.5M and again increases at a concentration of 0.75M and decreases again at 1M. The highest absorbance peak is at a concentration of 0.25M (Figure 1(a)). When the precursor solution has transformed into a thin film (FIGURE 1(b)), the absorbance value changed, except for 0.1M, where the absorbance remains the same, specifically 0.33. The absorbance value decreases as much as 86.4%, 46,5% and 82.5% for 0.25M , 0.75M and 1M, and increases as much as 21.4% for 0.5M.

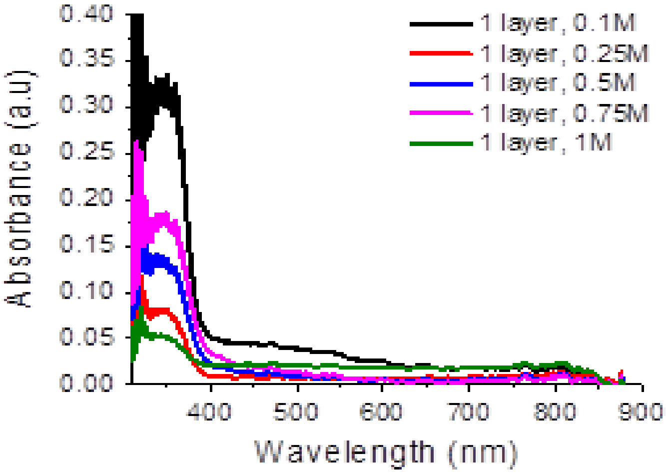
Based on the Beer-Lambert law, the absorbance directly proportional to the concentration, meaning that the higher the concentration, the higher the absorbance, and vice versa. However, in this study, we found that the increase in the absorbance value was not directly proportional to the increase in the concentration of zinc acetate, but there was an optimum value for absorbance at a concentration of 0.25M (for precursor solution) and 0.1M (for a thin film).

From the estimated gap energy value using the Tauc method, we discovered that the ZAD concentration does not affect the bandgap value, where the bandgap obtained is 3.21 eV, 3.24 eV, 3.20 eV, 3.19 eV and 3.20 eV for concentrations of 0.1M, 0.25M, 0.5M, 0.75M, and 1M, respectively.

Result for the measurement of the absorbance spectrum in a thin film for the concentration of Zinc acetate dihydrate of 0.1M, 0.25M, 0.5M, 0.75M, and 1M with different variations of layer, displayed in FIGURE 2. The absorbance of ZnO thin film increased by its number of layers. The thicker the layers, the higher the absorbance, because the sample becomes less transparent due to the more the layers formed and eventually increase the number of atoms in a thin film that absorbing the light. From the five concentration variations, the lowest absorbance value obtained at 0.1M.

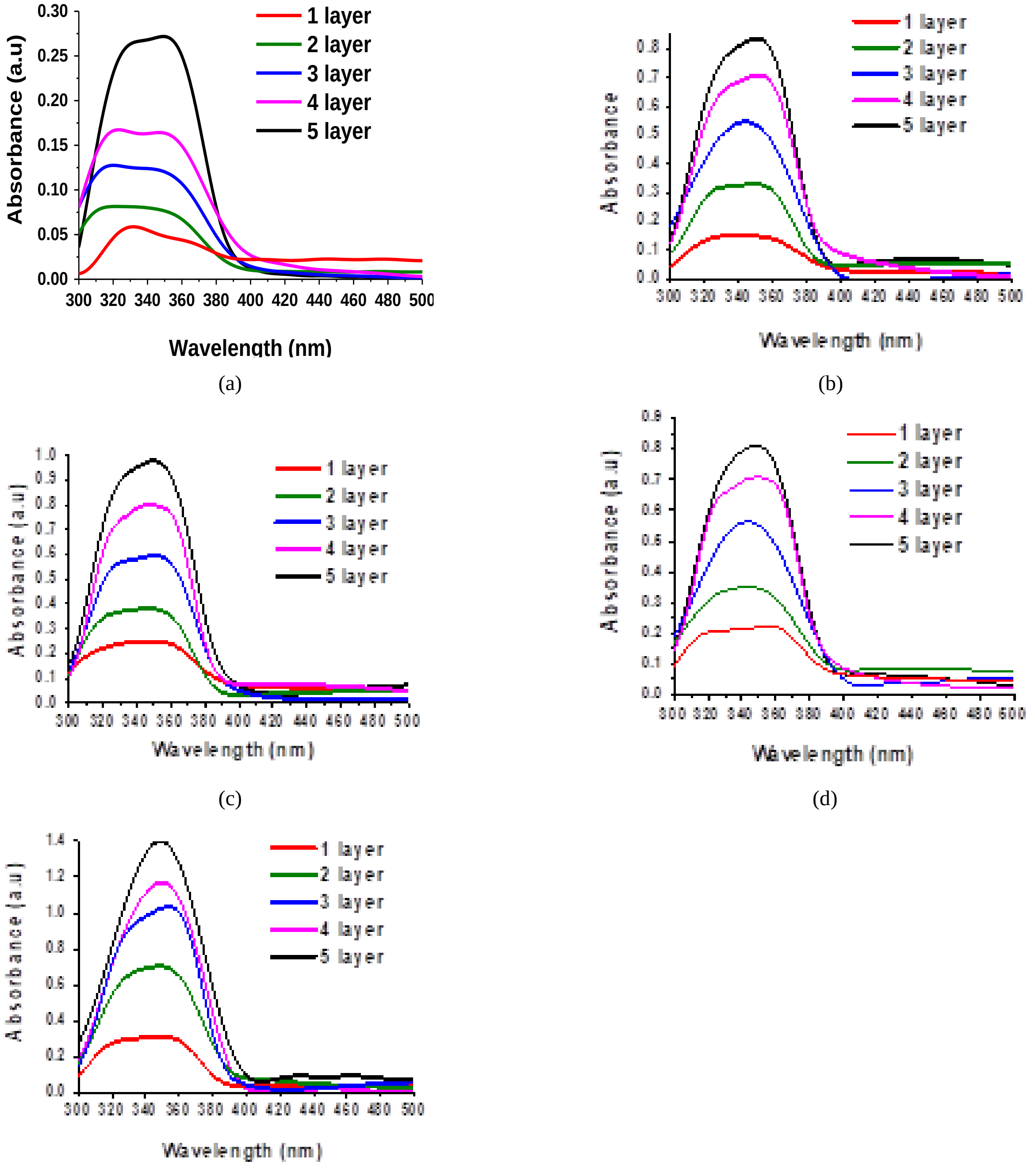


(a)



(b)

FIGURE 1. The absorbance spectrum of (a) ZnO precursor solution and (b) ZnO thin film for the concentration of 0.1M, 0.25M, 0.5M, 0.75M and 1M.



(a) (b)

(c) (d)

(e)

FIGURE 2. Absorbance spectrum for the concentration of (a) 0.1M, (b) 0.25M, (c) 0.5M, (d) 0.75M and (e) 1M with varied layers.

Transmittance Spectrum

FIGURE 3(a) shows the transmittance spectrum of precursor solutions with varying concentrations. Although visibly all the precursor solutions look transparent, the transmittance value turns out to be different. The precursor solution with concentrations of 0.1M, 0.5M, and 0.75M has almost the same transmittance, correctly 94.1%, 95.8%, 94.7%, respectively. The average transmittance from the former three, decreased as much as 13% at 1M, which is

82.2%. Precursor solution with a concentration of 0.25M has the lowest transmittance of 62.8%. This result is in good agreement with the absorbance spectrum measurement results for the precursor solution shown in FIGURE 1(a), where the highest absorbance value is obtained for samples with a concentration of 0.25M so that it has the lowest transmittance value compared with other concentrations, which is also supported by the following equation:

$$T = Be^{-\alpha t} \tag{2}$$

where T is the transmittance, B is a constant (B ~ 1), α is the coefficient of absorbance, and t is the thickness of the sample. If the thickness of the sample is fixed (in this case, the thickness of the plastic cuvette), the transmittance will decay exponentially with the absorbance coefficient, or in other words, if the absorbance is high, the transmittance is low.

Next to see was the effect of structural changes from amorphous to nanocrystalline structures after the precursor solution deposited on a glass substrate followed by a heating process in FIGURE 3(b). The transmittance of 0.1M decreases as much as 17.8% from the precursor solution to the thin film as the absorbance increase (FIGURE 1(b)). The transmittance also reduced as much as 7.2% and 11.6% for 0.5M and 0.75M, respectively. Meanwhile, the transmittance rises as much as 55.7% and 15.8% for 0.25M and 1M, respectively. Transmittance changes might be attributed to the change in shape from amorphous to crystal, together with the loss of the contribution of solvents and other additives.

The transmittance escalation in 0.25M, from 62.8% in the form of the solution to 97.7% after becoming a thin layer, was also caused by the absorbance value being small after being in the form of a thin layer, namely from 0.58 to 0.1 for one coating. In samples with the same thickness (one-time coating), the highest transmittance value obtained on thin films with a concentration of 0.25M.

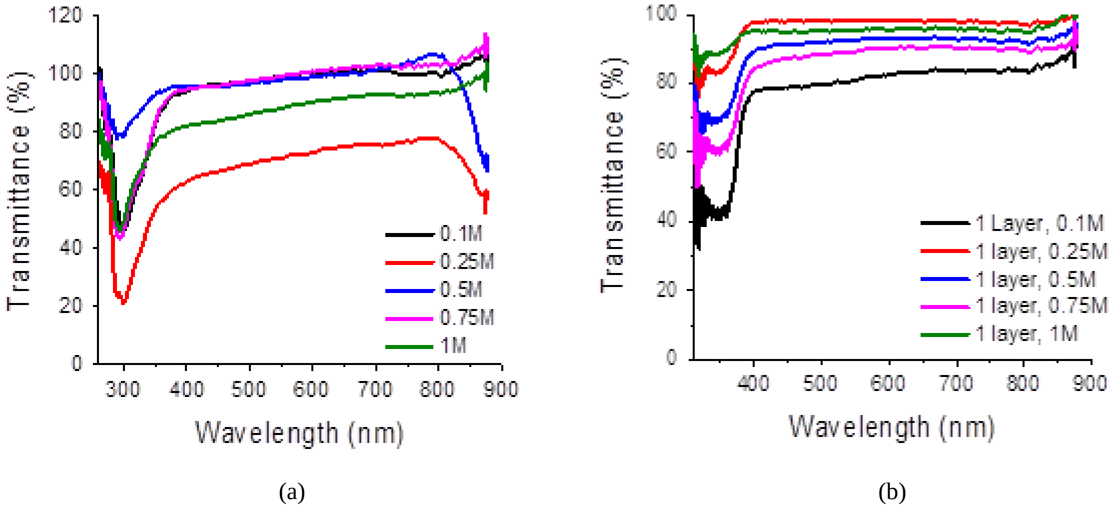


FIGURE 3. Transmittance spectrum of (a) ZnO precursor solution and (b) ZnO thin film with different concentrations.

From FIGURE 4, added the layer thickness until five times layering does not significantly reduce the transparency of the ZnO thin film, whose transmittance only degradated as much as 2.8%. This result indicated that the thickness problem would not be a significant issue when it applied to a particular device.

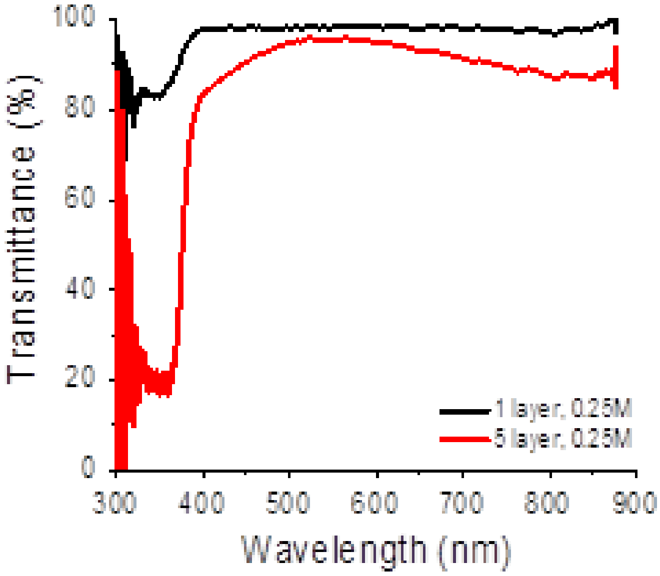


FIGURE 4.Transmittance spectrum of ZnO thin film with different layer number and same concentration

Effect of thin-film deposition parameters on the crystallite size and optical properties

XRD characterization

For XRD measurements, nine types of samples made from a solution with a ZAD concentration of 0.25M, namely sample 1 (A, B, C) made at speeds of 1230rpm for 10s, 15s, and 30s respectively. Furthermore, sample 2 (A, B, C) made with a speed of 2500rpm for 10s, 15s, and 30s. Then the last sample is sample 3 (A, B, C) made at 3200rpm for 10s, 15s, and 30s. The other samples are not good (white and not transparent), so the XRD spectrum displayed is 1C, 2C, 3A, and 3C samples. FIGURE 5 shows the XRD diffractogram pattern of the four samples deposited using a spin coater.

We can see that sample 1C (which has) four diffraction lines (peaks) has the most cell units detected by XRD devices. As the rotating speed escalates (1C, 2C, 3C), the number of cell units detected by the XRD device down to two diffraction lines. The reduced number of cell units detected related to the thickness of the resulting thin layer where the thicker the resulting layer, the more the number of atoms that can arrange one cell unit. The thickness of this layer is affected by the spin coater rotational speed, the faster the rotation, the resulting layer will be thinner, as shown by the following equation.

$$t \propto \frac{1}{\sqrt{\omega}} \qquad (3)$$

Furthermore, the diffractogram pattern further used to estimate the size of the synthesized ZnO crystallite using equation (1). TABLE 1 shows the results of ZnO crystal grain size calculations. The crystalline size of the synthesized ZnO has a size range between 30-56nm. Several factors can influence the size of the crystals formed from the synthesis process of a nanocrystalline. According to [18], heating with variations in calcination temperature affects the size of the crystal produced. The higher the temperature used in the calcination process, the greater the size of the crystals obtained.

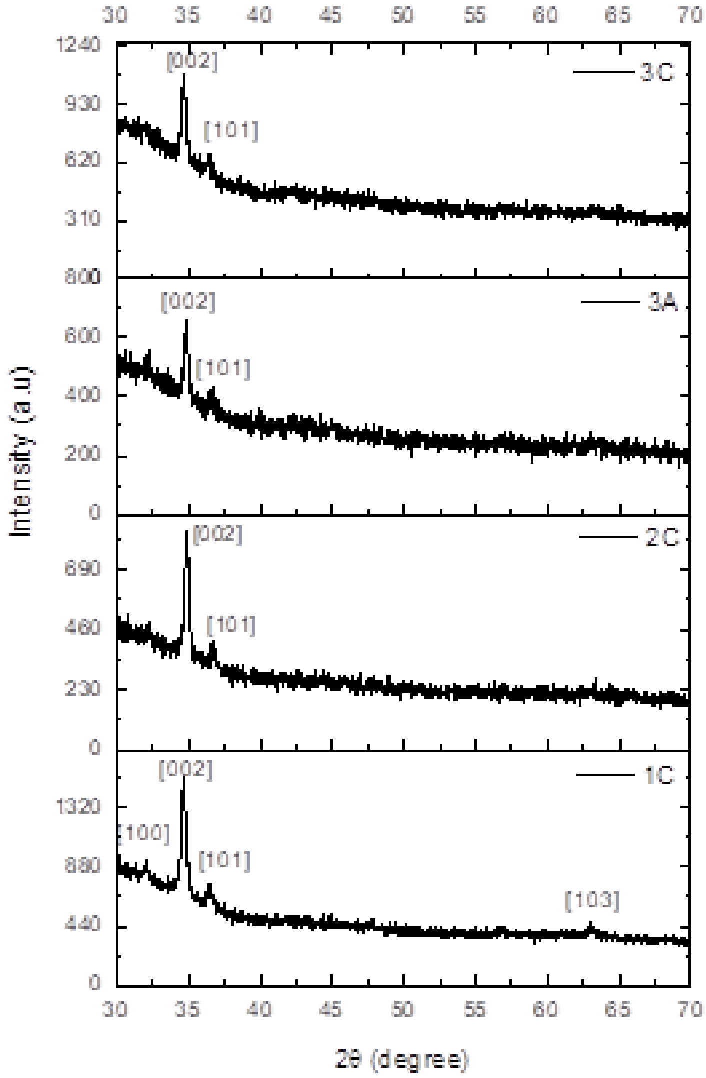


FIGURE 5. Diffraction pattern of twenty layers ZnO thin film prepared by the sol-gel method

In FIGURE 6, it appears that all the intensity of the orientation of the crystal plane decreases with increasing rotational speed (1C, 2C, and 3C). The higher the rotational speed, the greater the centrifugal force produced so that many ZnO precursor solutions dispersed out of the substrate. As a result, the thickness of the layer decreases. The intensity of diffraction lines related to the number of atoms in a unit cell. The thinner the ZnO layer produced, the smaller the number of atoms, therefore the intensity decreases.

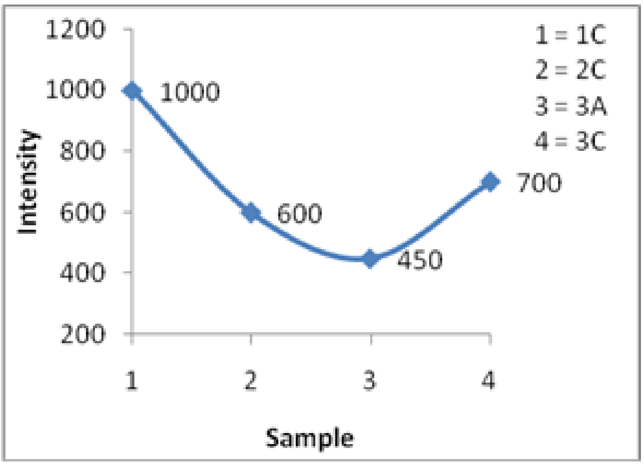


FIGURE 6. Peak intensity for different rotation speed and time deposition

TABLE 1. 2θ value and crystallite size of the maximum peak

No	Sample	Rotation Speed (rpm)	Time (s)	θ_{max} (◦)	d-spacing Exp (Å)	d-spacing Database (Å)	[hkl]	Crystalite size (nm)
1	1C	1230	30	31.81	-	2.807	[100]	30.98
				34.63	2.587	2.593	[002]	48.54
				36.34	2.461	2.469	[101]	48.02
				63.25	1.472	1.472	[103]	45.59
2	2C	2500	30	34.84	2.571	2.593	[002]	52.64
				36.65	2.448	2.469	[101]	27.33
3	3A	3200	10	34.86	2.571	2.593	[002]	56.96
				36.73	-	2.469	[101]	21.49
4	3C	3200	30	34.63	2.586	2.593	[002]	47.48
				34.46	2.465	2.469	[101]	35.00

Transmittance spectrum

We also measured the transmittance of the 20 layers ZnO thin film (FIGURE 7). The transmittance value varies with rotational speed and rotation time. Sample 1C has the lowest transmittance value of 67%. The transmittance value then increases with increasing speed and rotational time, which is 72%, 80%, and 83% for the 2C, 3A, and 3C samples, respectively. These results indicate that up to 20 times coating, the resulting ZnO thin film still shows fairly good transparency with transmittance above 80%, especially for samples 3A and 3C.

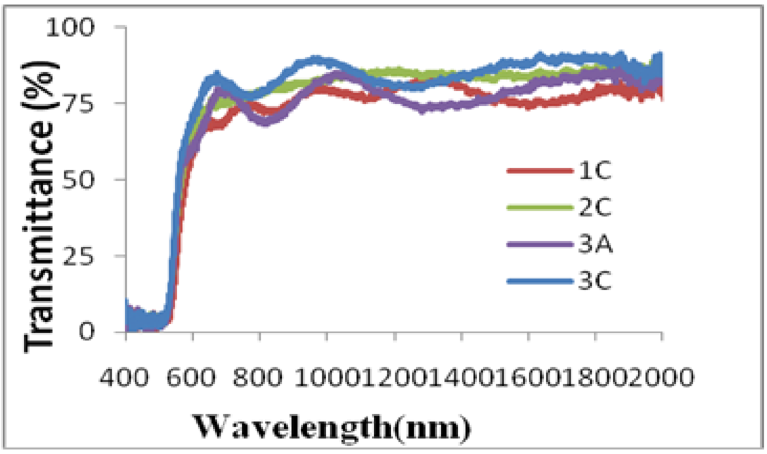


FIGURE 7. The transmittance of twenty layers of ZnO thin films for different rotation speed and time deposition

From the picture above, it concluded that the sample with the highest rotational speed and the longest rotating time, in this case, the 3C sample, produces thin films with better transparency. However, in terms of surface morphology, the 2C sample shows a smoother surface that is marked by a smooth transmission line without the appearance of interference fringes, as shown by samples 1C, 3A, and 3C.

CONCLUSION

From this research, we have been able to produce ZnO thin films with variations in concentration whose transmittance is above 80% or even reaches 97% so that the ZnO is a suitable candidate for use as an electron receiving layer in DSSC solar cells. As for the variation of spin coating speed and spin time, the sample with the highest rotational speed and the longest rotate time in this case the 3C sample, produces thin films with better transparency. However, in terms of surface morphology, the 2C sample shows a smoother surface that is marked by a smooth transmission line without the appearance of interference fringes, as shown by samples 1C, 3A, and 3C. In order to be used as the electron transport layer in solar cells, one must choose the sample that results in higher transmittance, which is 0.25M, using the medium speed, namely around 2000 rpm, to produce a smoother surface.

ACKNOWLEDGEMENT

This work funded by the Ministry of Research and Technology, Directorate of Research and Community Service-Higher Education of Indonesia, through a national competitive research program – Basic Research 2019, with a contract number of 171/SP2H/LT/DRPM/2019 and 512g/UN29.20/PPM/2019.

REFERENCES

[1] L. Shruthi *et al.*, “Photocatalytic degradation and removal of heavy metals in pharmaceutical waste by selenium doped ZnO nanocomposite semiconductor,” *Journal For Research*, vol. 2, no. 5, 2016.

[2] M. Tan, G. Qiu and Y. P. Ting, “Effects on ZnO nanoparticles on wastewater treatment and their removal behavior in a membrane bioreactor,” *Biosource Technology*, vol. 185, pp. 125-133, 2015.

[3] Li X *et al.*, “Synthesis and morphology control of ZnO nanostructures in microemulsions,” *J. Colloid Interface Sci*, vol. 333, pp. 465-473, 2009.

[4] Lu CH and Yeh CH, “Emulsion precipitation of submicron zinc oxide powder,” *Mater Lett*, vol. 33, pp. 129-132, 1997.

[5] D. Chen, X. Ciao and G. Cheng, “Hydrothermal synthesis of zinc oxide powders with different morphologies,” *Solid State Commun*, vol. 113, pp. 363-366, 2000.

[6] F. A. Akgul, K. Attentkofer and M. Winterer, “Structural properties of zinc oxide and titanium dioxide nanoparticles prepared by chemical vapor synthesis,” *J. Alloy Compd*, vol. 554, pp. 177-181, 2013.

[7] X. Zhao *et al.*, “Acetate-derived ZnO ultrafine particles synthesized by spray pyrolysis,” *Powder Technol*, vol. 100, pp. 20-23, 1998.

[8] H. Bennebal et al., “photocatalytic degradation of phenol and benzoic acid using ZnO powders prepared by sol-gel process,” *Alex. Eng. J*, vol. 52, pp. 517-523, 2013.

[9] M. Ristic et al., “Sol-gel synthesis and characterization of nanocrystalline ZnO powders,” *J. Alloy Compd*, vol. 39, pp. L1-L4, 2005.

[10] K. G. Kanade *et al*., “Effect of solvents on the synthesis of nanosize zinc oxide and its properties,” *Materials Research Bulletin*, vol. 41, no. 3, pp. 590-600, 2006.

[11] B. Manikandan *et al*., “Properties of sol-gel synthesized ZnO nanoparticles,” *J Mater Sci: Mater Electron*, vol. 29, no. 11, pp. 9474-9485, 2018.

[12] O. Mauit *et al*., “Growth of ZnO: Al by atomic layer deposition: Deconvoluting the contribution of hydrogen interstitials and crystallographic texture on the conductivity,” *Thin Solid Films*, vol. 690, p. 137533, 2019.

[13] M. Verde *et al*., “Electrophoretic Deposition of Transparent ZnO Thin Films from Highly Stabilized Colloidal Suspensions,” *J. Colloid and Interface Sci*, vol. 373, no. 1, pp. 27-33, 2012.

[14] T. Ratana *et al*., “The wide bandgap of highly oriented nanocrystalline Al-doped ZnO thin films from sol-gel dip coating,” *J. Alloy Compd*, vol. 470, no. 1-2, pp. 408-412, 2009.

[15] Y. Natsume and H. Sakata, “Zinc oxide films prepared by sol-gel spin-coating,” *Thin Solid Films*, vol. 372, no. 1-2, pp. 30-36, 2000.

[16] A. Aprilia *et al*., “Influences of dopant concentration in sol-gel derived AZO-layer on the performance of P3HT PCBM based inverted solar cells,” *Solar Energy Materials and Solar Cells*, vol. 111, pp. 181-188, 2013.

[17] W. O. S. Arsyad *et al*., “Non-ohmic resistance effects of the AZO and TiZO as a blocking layer in dye-sensitized solar cells (DSSCs),” *Journal of Nonlinear Optical Physics & Materials*, vol. 27, no. 2, p. 1850019, 2018.

[18] S. Mashid et al., “Synthesis of TiO2 nanoparticles by hydrolysis and peptization of titanium isopropoxide solutions,” *Semiconductor Physics, Quantum Electronics and Optoelectronics*, vol. 9, no. 2, pp. 65-68, 2006.