PAPER • OPEN ACCESS

Sintering temperature effect on optical properties of zinc oxide thin film on glass substrate prepared by sol-gel spin coating method

View the article online for updates and enhancements.

Sintering temperature effect on optical properties of zinc oxide thin film on glass substrate prepared by sol-gel spin coating method

L Rumiyanti[1,*]**, D Aryanto**[2]**, S Garcia**[3]** , Syafriadi**[4]** , I Firdaus**[5]

[1]Department of Physics, Faculty of Mathematics and Natural Sciences, University of Lampung, Jl. Sumantri Brojonegoro no 1, Bandar Lampung, Indonesia
[2]Indonesian Institute of Science - LIPI, Research Center of Physics, Puspitek Serpong, Tangerang, Indonesia

email: lenirumiyanti@fmipa.unila.ac.id[1,*]

Abstract. Research on the optical properties of the ZnO thin film with the use of sol-gel method and spin coating method using 0.5 M concentrate solution of $(Zn(CH_3COO)_2 \cdot 2H_2O)$ and 30 mL isopropyl alcohol as a solvent has been carried out. The production process of ZnO solution and the fabrication of the thin film with the optical properties test of the thin film are included in the scope of this research. UV-Vis Spectroscopy is used to obtain the transmittance and absorbance values on each wavelength and the band gap energy value using the Tauc Plot method. The transmittance value obtained is directly proportional with the temperature. The absorbance value obtained is inversely proportional with the temperature due to higher temperature causes the reaction rate to become faster and in turn causes the absorbance value to become lower. The band gap energy value obtained is on the range of 3.23 eV – 3.27 eV and it fit with the literature.

1. Introduction

Zinc oxide (ZnO) is an inorganic compound and a type-n semi-conductor material with band gap energy of 3.2 eV to 3.3 eV on room temperature. It is tough and brittle on most temperature but could be forged between 100°C to 150°C and above 210°C [1]. It is an important semi-conductor material because it has wide band gap energy.It is used in several applications such as transparent conductor, solar cell windows, gas sensor and photovoltaic instrument [2]. Zinc oxide (ZnO) can have piezoelectric property which is caused by its wurtzite crystal structure. The commonly used materials in material science especially on thin film research are SnO_2, WO_3, TiO_2, ZnO, and others. This research used ZnO because it has high photo-catalyst efficiency in regard of other semi-conductor materials. It high photo-catalyst efficiency is caused by the generation of hydrogen peroxide (H_2O_2) [3-5].

Zinc oxide (ZnO) thin film can be synthesized by both vacuum based method such as pulsed laser deposition (PLD), chemical vapor deposition (CVD), sputtering, laser ablation and spray pyrolysis [5] and solution based method such as chemical bath deposition, sol-gel process, electro deposition and hydrothermal [6]. This research used the sol-gel process of solution based method to synthesize the

material. The sol-gel process is a solution based method that can produce good, simple and low cost small or wide thin film [7]. It can produce material with high homogeneity and with desired controllable material composition [8]. A "sol" is a colloidal solution which has dispersed solid phase and liquid phase as its dispersing agent [9]. Gelation or "gel" is a growth process through polymer condensation or particle grouping [10].
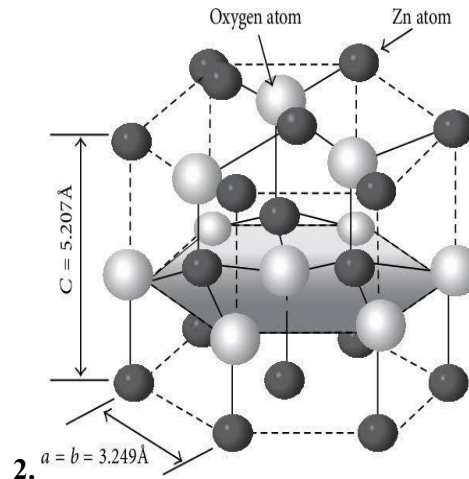

Figure 1. Crystal structure of ZnO

This research chooses the spin coating method for thin film growth processing. It is an easy and fast method. The thin film made by this method has a high homogeneity. The thickness of the thin film can be controlled using time and spin speed of the spin coater [11]. The spin coating process consists of four stages which is deposition, spin up, spin off and evaporation [12].

The knowledge of electrons on a crystal structure which is arranged inside the energy bandandis separated by energy space of non-orbital electrons is needed to know the value of the electric conductivities. This energy space of non-orbital electrons is called a band gap and is the result of the interaction of the electron conductivity with the core ion of the crystal structure [13]. A plot of $(\alpha h v)^2$ versus hvmade by extrapolating the linear part of the curve to the zero absorption line gives the value of the band gap energy for a direct allowed transition [14].

Ultraviolet-visible (UV-Vis) spectroscopy is consist of a spectrometer which produce light spectrum with specific wavelength and a spectrophotometer which is an instrument for calculating the intensity of transmitted or absorbed light spectrum [15]. This research used varied sintering temperature of 300°C, 400°C and 500°C to ascertain the effect of temperature towardthe optical properties of zinc oxide thin film on glass substrate using the UV-Vis spectrophotometer.

2. Materials and methods
Digital scale, beaker, spatula, micropipette, fume hood, magnetic stirrer, ultrasonic cleaner, spin coater and desiccator are the instrument used in this research. This research also used zinc acetate dihydrate $(Zn(CH_3CO_2)_2 \cdot 2H_2O)$, isopropyl alcohol (C_3H_8O), ethanolamine (C_2H_7NO), hydrochloric acid (HCl), ethanol (C_2H_5OH), acetone (C_3H_6O) and distilled water (H_2O) as its material. The research scheme can be seen in Figure 2. This research consists of three main stages which is the production of ZnO solution, the fabrication of ZnO thin film and the optical properties test.
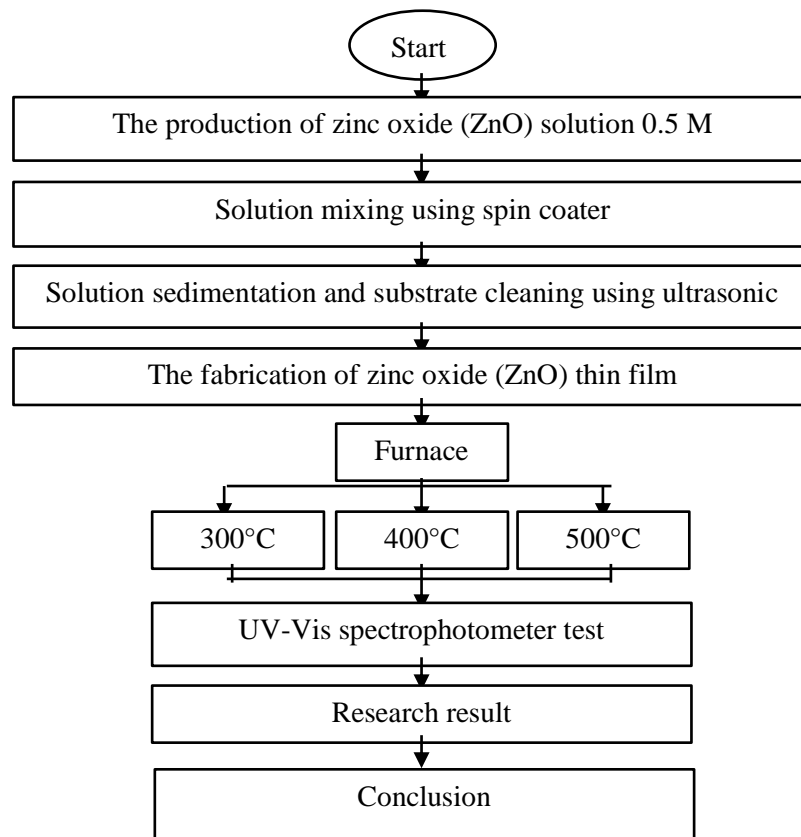
Figure 2. Research scheme

The production of ZnO solution consists of two parts which is the solution mixing andthe solution sedimentation. For the first parts, 0.5 M zinc acetate dihydrate($Zn(CH_3CO_2)_2 \cdot 2H_2O$) is mixed with isopropyl alcohol (C_3H_8O) and stirred using magnetic stirrer with 3000 Rpm setting on room temperature until it attain homogeneity. For the second parts, ethanolamine (C_2H_7NO) was dripped into the solution until it became colorless or transparent on 70°C for 1 hour and then settled it for 24 hours for the completion of solution sedimentation process.

The fabrication of ZnO thin film is done by coating the substrate using the spin coating method. It consists of three parts which is the substrate cleaning, the spin coating process and the varied sintering temperature conditioning. For the first parts, the substrates are cleaned using ultrasonic cleaner mixed with acetone (C_3H_6O) for 5 minutes and then mixed again with ethanolamine (C_2H_7NO) and distilled water for 5 minutes. For the second parts, the cleanedsubstrates coated inZnO solution are placed on the spin coater with 4000 Rpm setting. The coated substrates then transferred on the hot plate for 5 minutes on 110°C and then repeat the whole process for a second time. For the third parts which is the varied sintering temperature conditioning, the ZnO thin film then placed inside the furnace for sintering on 300°C, 400°C and 500°C temperature for 1 hour.

The optical properties test of the ZnO thin film is done using UV-Vis spectrophotometer. It is used to acquire the transmittance value, the absorbance value and the band gap energy using the Tauc plot method.

2.1 Absorbance value calculation
The relation between absorption coefficient (α)and incoming photon energy (hν) can be written as;

$$(ahv)^{\frac{1}{n}} = b(hv - Eg) \tag{1}$$

hv is photon energy, b is a constant, Eg is optical band gap energy of the semi-conductor material and n is an exponent which depend on the type of the transition inside the material. For a direct allowed transition n = ½ and for indirect allowed transition n = 2. The absorption coefficient (α) is calculated using the absorbance data or transmittance data for each wavelength as shown in the Beer-Lambert equation;

$$I = I_0 \exp(-\alpha t) \tag{2}$$

I is the light intensity transmitted through the sample film, I_0 is the incoming light intensity and t is the thickness of the sample film. Absorbance value (A) is written as;

$$A = \log \frac{10}{I} = -\log T \tag{3}$$

2.2 Band gap energy calculation

Optical band gap energy of the thin film can be calculated using Urbach equation;

$$\alpha hv = C(hv - Eg)^{\frac{1}{2}} \tag{4}$$

C is a transitional characteristic parameter of photon energy, h is Planck's constant, and v is the light frequency. E is optical band gap energy of the thin film which can be written as;

$$E = hv = \frac{hc}{\lambda} \tag{5}$$

h is Planck's constant ($6.262 \cdot 10^{-34}$ Js), c is the light speed constant ($3 \cdot 10^8$ m/s) and λ is the light wavelength.

3. 3. Result and discussion

3.1 Material synthesis

This research used the varied sintering temperature of 300°C, 400°C and 500°C to ascertain the effect of temperature towards the optical properties of ZnO thin film. It consists of three main stages which are the production of ZnO solution, the fabrication of ZnO thin film and the optical properties test using UV-Vis spectrophotometer. The production process of ZnO solution is done using 0.5 M concentrate solution of zinc acetate dihydrate ($Zn(CH_3CO_2)_2 \cdot 2H_2O$). The fabrication of ZnO thin film is consists of three parts which is the substrate cleaning, the spin coating process and the varied sintering temperature conditioning. The substrates are cleaned using acetone (C_3H_6O) and the spin coating process is done using the spin coater with 4000 Rpm setting. The varied sintering temperature conditioning is done by sintering the substrate using the furnace on 300°C, 400°C and 500°C for 1 hour. The optical properties test is done using the UV-Vis spectrophotometer to acquire the transmittance value, the absorbance value and the band gap energy using the Tauc plot method. The differences of the thin film pattern in this research can be seen in Table 1.

Table 1. The result of the fabrication of ZnO thin film

3.2 Transmittance value

The transmittance value graph of ZnO thin film acquired using UV-Vis spectrophotometer can be seen in Figure 3. It is shown from the graph that at 240 nm to 360 nm wavelength there is an inclinein transmittance value curve. The highest transmittance value occurred at 80% for thin film sintered in 300°C, at 77.5% for thin film sintered in 400°C and at 85.9% for thin film sintered in 500°C. The result of the transmittance value of ZnO thin film can be seen in Table 2. The transmittance value obtained is directly proportional with the sintering temperature.
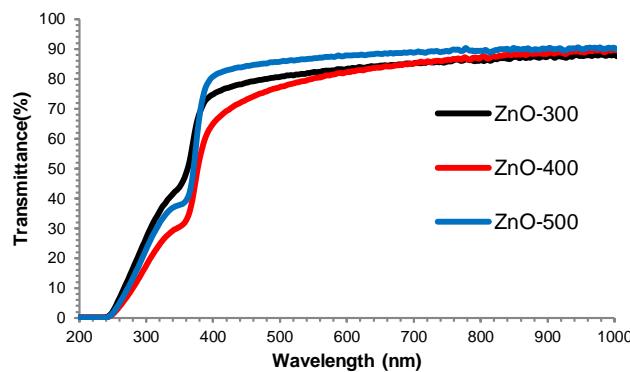

Figure 3. The transmittance value of ZnO thin film graph

Table 2. The transmittance value of ZnO thin film result

Temperature (°C)	Highest Transmittance Value (%)
300°C	80
400°C	77.5
500°C	85.9

It shown in Figure 3 that at 360 nm to 1000 nm wavelength the transmittance value appears to be constant. The UV light spectrum has a wavelength around 400 nm. The wavelength from 360 nm to 1000 nm has higher chance to be transmitted through the thin film because of it. The transmittance value appears to be constant because the UV light spectrum is being transmitted through the thin film. Absorbance Value

The absorbance value graph of ZnO thin film acquired using UV-Vis spectrophotometer can be seen in Figure 4. It is shown from the graph that at 360 nm wavelength there is a decline in absorbance value curve. The lowestabsorbance value occurred at 5.4% for thin film sintered in 300°C, at 4.5% for thin film sintered in 400°C and at 4.3% for thin film sintered in 500°C. The result of the absorbance value of ZnO thin film can be seen in Table 3. The absorbance value obtained is inversely proportional with the sintering temperature. It isinversely proportional due to highersintering temperature causes the reaction rate of the material to become faster.The faster reaction rate of the material in turn causes the absorbance value to become lower.
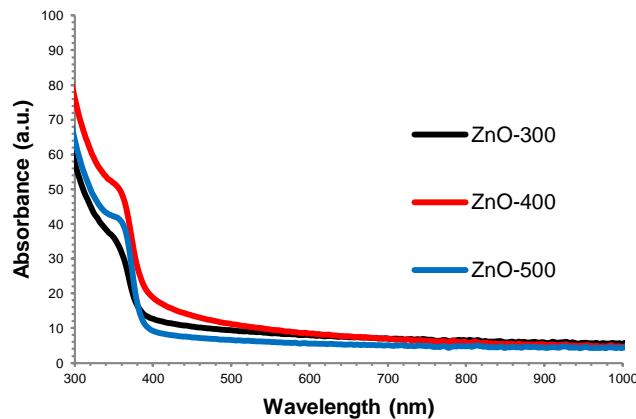

Figure 4. The absorbance value of ZnO thin film graph

Table 3. The absorbance value of ZnO thin film result

Temperature (°C)	Lowest Absorbance Value (%)
300°C	5.4
400°C	4.5
500°C	4.3

It shown in Figure 4 that at 360 nm to 1000 nm wavelength the absorbance value appears to be constant. The UV light spectrum has a wavelength around 400 nm. The wavelength from 360 nm to 1000 nm has lower chance to be absorbed by the thin film because of it. The absorbance value appears to be constant because the UV light spectrum is not being absorbed by the thin film.

3.3 Band gap energy value
The band gap energy calculation of semi-conductor material needs to be done. It gives implication to the differences in the material properties. The properties depend on the absorption coefficient at each photon frequency [16]. The band gap energy value of ZnO thin film is obtained by plotting the absorbance value data using direct allowed transition equation [17].

The graph relation between $(\alpha h\nu)^2$ and $(h\nu)$ can be seen in Figure 5. The band gap energy value is shown by intersecting the curve shown in the graph with the horizontal axis. The band gap energy is the energy that needed by the electron to move from the valence band to the conduction band. Zinc oxide is a compound that has band gap energy value around 3.2 eV to 3.3 eV,it has electrical and optical properties and mostly used as photoconductor and integrated sensor [18]. The band gap energy value obtained is inversely proportional with the sinteringtemperature. It is on the range of 3.23 eVto 3.27 eV which is shown in Table 4. This value is in accordance with the existing literature.
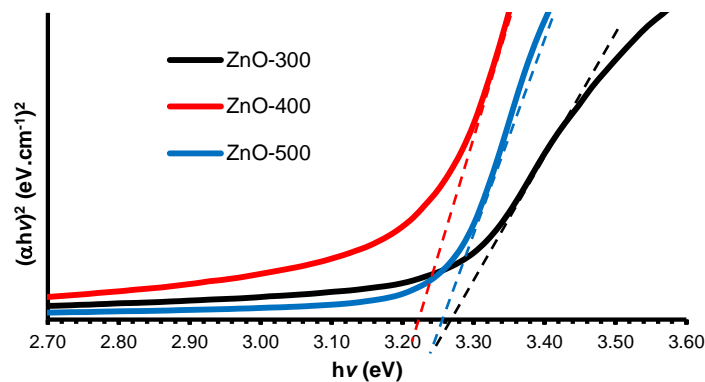
Figure 5. The band gap energy value of ZnO thin film graph

Table 4. The Tauc plot result of ZnO thin film

Temperature (°C)	Band Gap Energy (eV)
300°C	3.27
400°C	3.22
500°C	3.26

The band gap energy became lower along with the increase of the absorbance value. The higher the energy that the material absorbs caused the band gap energy value to decrease. The decrease is relatively small which is around 0.1 eV to 0.5 eV. The band gap energy graph obtained is smooth because it uses the same molarity which is 0.5 M for each sample. If the band gap energy value became smaller there might be more chances for the electrons to move from the valence band to conduction band and in turn changes the properties of the thin film to be more conductive.

4. Conclusions

The conclusion based on this research is as follow. The transmittance value obtained is directly proportional with the sintering temperature. The highest transmittance value is 85.9% at 500°C sintering temperature. The absorbance value obtained is inversely proportional with the sintering temperature.It is inversely proportional due to higher sintering temperature causes the reaction rate of the material to become faster.The faster reaction rate of the material in turn causes the absorbance value to become lower. The lowest absorbance value is 4.3% at 500°C sintering temperature.The band gap energy value obtained is inversely proportional with the sintering temperature. The band gap energy value obtained is on the range of 3.23 eV to 3.27 eV.

5. References

[1] Bednarek P. 2010. *Ceramic Materials – Forming Methods and Properties of Final Elements*. Warszawa. Warsaw University of Technology.
[2] Bizarro M, Sanches A, Garduno W, Alonso J, dan Ortiz A. 2011. Synthesis and Characterization of ZnO and ZnO:Al by Spray Pyrolysis with High Photocatalytic Properties. *Catalysis Today*. **2** 127
[3] Hoffmann A, Claus F, Bruno K, Andreas W, dan Johannes M. 2010. Zinc Oxide: From Fundamental Properties Towards Novel Application. *Springer*. **15** 9
[4] Gupta P, Shishoda, dan Kapoor A. 2010. Non-Crystalline Solids: Glasses and Amorphous Solids. *Journal Of Non Crystallin Solids.* **2** 31

[5]   Hafdallah A, Yanineb F, Aida M, dan Attaf N. 2011. In Doped ZnO Thin Films. *Journal of Alloys and Compounds*. **509** 7267

[6]   Bu I. 2014. Sol-Gel Production of Alumunium Doped Zinc Oxide Using Alumunium Nitrate. *Materials Science in Semiconductor Processing*. **27** 19

[7]   Li Y, Meng J, Ziqiang X, dan Cheng H. 2014. Al-Doping Effects on Structure and Optical Properties of ZnO Nanostructures. *Materials Science*. **9** 260

[8]   Bhushan, B. 2007. *Handbook of Nanotechnology*. Ohio State University. Columbus USA.

[9]   Paveena L, Vittaya A, Supapan S, dan Santi M. 2010. Characterization and Magnetic Propetis of Nanocrystalline $CuFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$ Powders Prepared by Aloe Vera Extract Solution. *Current Applied Physics*. **11** 101

[10]   Brinker C. 1990. *Sol-Gel Science*. London. Academic Press

[11]   Luurtsema G. 1997. Spin Coating for Rectangular Substrates (Thesis). University of California. Barkeley. **2** 7

[12]   Hellstrom S. 2007. *Basics Models of Spin Coating. Submitted As Coursework For Physics*. California. Standford University

[13]   Kittel C. 1996. *Introduction to Solid State Physics*. New York. John Wiley and Sons

[14]   Firdaus C, Rizam M, Rusop M, dan Hidayah S. 2012. Characterization of ZnO and ZnO: TiO2 Thin Films Prepared by Sol-Gel Spray-Spin Coating Technique. *Original Research Article Procedia Engineering*. **41** 1367

[15]   Khopkar S. 1990. *Konsep Dasar Kimia Analitik*. Jakarta. Universitas Indonesia Press.

[16]   Mikrajuddin A, dan Khairurrijal. 2010. Karakterisasi Nanomaterial. *Jurnal Nanosains dan Nanoteknologi*. **2** 9

[17]   Kusnandar A, Rachmawati H, Budi P, dan Suhandono S. 2013. Curcumin Nanoemultion for Transdermal Application: Formulation and Evaluation. *Proceedings Workshop Nanotechnology*. **1** 560

[18]   Miller G. 1959. Use of Dinitrosalicylic Acid Reagent for Determination of Reducing Sugar. *Analytical Chemistry*. **31** 426