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INFLUENCE OF CONCENTRATION AND POST-HEATING TO THE CRYSTAL SIZE AND OPTICAL PROPERTIES OF ZnO THIN FILMS

Nurdin Siregar[1,2], **Eddy Marlianto**[2,3], **Saharman Gea**[23] and **Nurul Taufiqu**[4]

[1]*Physic Department Faculty of Mathematic and Natural Science of Unerversitas Negeri Medan*
[2]*Physic School of Post Graduate Universitas Sumatera Utara*
[3]*Faculty of Mathematic and Natural Science of Universitas Sumatera Utara*
[4]*Research center of science and technology*
Email:siregarnurdin@rocketmail.com

ABSTRACT

ZnO thin films have been successful synthetized with sol-gel method based on the variation solution concentration and post-heating. *Zinc acetat dehydrate* $Zn(CH_3COOH)_2$ $2H_2O$, *isopropanol* dan diethanolamine (*DEA*) respectively as base material, solvent and stabilizer. *Zinc acetat dehydrate* $Zn(CH_3COOH)_2$ $2H_2O$ dissolved in isopropanol in a variation of the concentration of the moleculle, 0,6 M; 0,7 M dan 0,8 M then stabilized with diethanolamine (*DEA*). The molar ratio between the DEA and ZnAc is 1 : 1. Mixing process using reflux technique for controlling the rate of reaction and isolate the synthesis of outside air humidity. ZnO thin film manufacturing is done over a glass substrate by *spin-coating* technique with a rotation speed of 5000 rpm, for 30 seconds to get a thin film of good and homogeneous. Calcination is done by *pre-heating* to 300^0C and *post-heating* temperature variations are 500^oC; 550^oC; 650^oC . Forming a thin film composed of ZnO particles were observed along with the heating process (*pre-heating* and *post-heating).* Characterization of ZnO thin films made with *X-Ray Diffraction* (*XRD*) and UV-Vis to determine the structure, size and optical properties of ZnO crystal ZnO thin films. *XRD* analysis shows the crystal structure of hexagonal-shaped ZnO thin films with the smallest size of 25,4 nm for concentration 0,6 M and 32,4 nm for post-heating 550^oC. Based characterization of UV-Vis that ZnO thin films have the highest transmittance 58,86 % to 0,7 M concentration with the energy band gap of 3,16 eV and the highest transmittance of 51,87% for the *post-heating* to 600°C with energy band gap og 3,14 eV.

Keywords : *Crystal size, the optical properties of ZnO thin films, concentration and post-heating.*

INTRODUCTION

Nanoparticle are microscopic particles that have a size in the nanometer scale is < 100 nm. Nanoparticles into a very interesting study , because when a substance/material has been in the form of nanoparticles, the particles usually have different properties from the properties of previous material. Nanometer-sized materials have a number of chemical or physical properties that are superior to large size material (bulk). (Dian , 2009, CR Vestal et al, 2004 , SM Yusuf . Et al, 2006 and Cao, Guozhong, 2004). The properties can be altered by means of controlling the size of the material, setting the chemical composition, surface modification, and control inter-particle intaksi (Omar, 1975) .

In materials science in particular ZnO is an n-type semiconductor material group II - VI with width band gap energy of 3.37 eV and a binding energy of excitation of 60 mV at room temperature (CT Chen, et al, 2009, Tamiko, et al , 2003, Jing. SH and Ching . 2008). ZnO is one type of metal oxide which is one of the manufacture of thin films occupies a unique position among a number of other materials , due to its optical and electrical properties as well as ease the process of deposition , as well as the availability of abundant and not easily react chemically with other elements. Moreover , ZnO has emission properties near UV light , photocatalysts, high conductivity and transparency . ZnO thin film as base material that is much in demand because it has several advantages in application, especially in the field of sensors , solar cells and nanodevice. (Boning, 2007) .

Thin film of zinc oxide (ZnO) lately has been widely studied and used for a variety of important applications such as light-emitting devices, solar cells, gas sensors, flat panel displays etc. This application is based as pulling characteristics of ZnO as the energy gap width , direct optical transitions etc. One of the interesting properties are owned by ZnO crystal formation can occur at temperatures below 400^oC, of course depending on the type of deposition and the solvent used . ZnO thin films can be synthesized by several methods such as molecular beam epitaxy (Changzheng W , 2009), the RF magnetron sputtering (Sungyeon Kim , 2006) , pulsed laser deposition (Zhu, 2010), spray pyrolysis (Gumus C. , et al , 2006), chemical bath deposition (Muhammad M. Ali, 2011) , physical vapor deposition (George , 2010), and the method of sol - gel spin coating (Ilican , 2008). Synthesis of thin films by sol- gel method spin coating has several advantages such as low cost, do not use a vacuum chamber with a high , homogeneous composition, thickness and microstructure can be controlled quite well , so this method is widely used in the manufacture of thin film (Cheng , 2004). Method of sol - gel spin coating is a combination of physical and chemical methods which are used to make thin films of polymer materials deposited on the surface of the photoresist which flat-shaped silicon. After the solution *(sol - gel)* was dropped on the substrate, the rotational speed is set by the centrifugal force to produce a homogeneous thin film. Method of sol - gel spin coating is very easy and effective way to make thin films by just set the parameters of time and round speed and solution viscosity .

METHODOLOGY

Sol –Gel Preparation

Zinc acetate dehydrate Zn (CH3COOH $)_2$ $2H_2O$, isopropanol and diethanolamine (DEA) respectively as precursor materials, solvents and stabilizers . Zinc acetate dehydrate Zn (CH3COOH $)_2$ $2H_2O$ dissolved in isopropanol with a solution of 0.6 M The concentration variations; 0.7 M and 0.8 M and then stabilized with diethanolamine (DEA). The molar ratio between the DEA and ZnAc is 1 : 1. Mixing process using reflux technique for controlling the rate of reaction and isolate the process of synthesis of the outside air humidity. Heating done on magnetic strierr over a temperature range of 60°C – 85°C with a rotation speed of 60 rpm and about 60 minutes long warming up in get a clear solution and transparent. At this stage liquid gel formed consisting of acid compounds derived from ZnAc particles are dissolved , along with the water. ZnAc dissolved have very small ears so that the solution looks clear. The solution was then cooled to room temperature to form a gel which is rather thick .

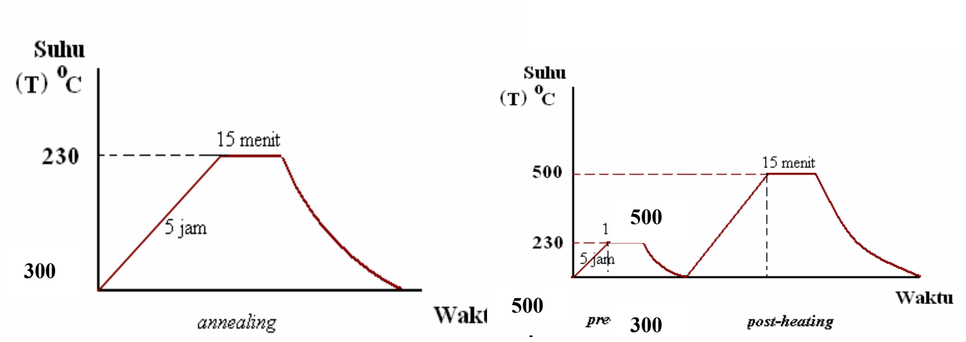
Coating Method

The Rotation speed in the manufacturing of ZnO films by spin coating technique at 5000 rpm within 30 seconds to get the best coating, flat, and homogeneous . The coating is performed for 30 seconds , for the first 10 seconds are used as spin - up process with a low rotation speed of 1000 rpm which aims to spread the gel over the surfaces subtract , and then rotated at a speed of 5000 rpm for 20 seconds as a spin-off process which aims to form a regular layer with homogeneous thickness . After subtract surface evenly coated , then dried in a furnace at 100°C and held for 10 minutes . Furthermore, the second coating , third to fifth in the same techinque .

Pre-heating and Post-heating process

Pre - heating is done by using a tanur *(furnace)* ranging from room temperature to 300°C which increased gradually up to 300°C for 5 hours. Samples let stand for 15 minutes at a temperature of 300°C, then lowered slowly to room temperature. This stage serves to remove solvent water, isopropanol, and the acid groups , and facilitate change ZnOH into ZnO as heating (hydrolysis) .

Annealing or post - heating with temperature variations 500^{0}C, 550^{0}C, and 600^{0}C. The increasing of temperature is done slowly up to a temperature from 500^{0}C, 550^{0}C , and 600^{0}C for 5 hours . Samples were allowed to stand for 15 minutes at a temperature of 500^{0}C, 550^{0}C, 600^0 C and then the temperature is lowered naturally to return to room temperature. Post - heating function for the formation of crystalline ZnO particles. Expected crystals formed have a uniform orientation , and has a small grain size and minimize pores are formed. Sample heating stage to develop pre - heating (300^{0}C) and post - heating (500^{0}C) can be seen in Figure 1.



(a) (b)

Figure 1. The process of pre - heating and post - heating . Increased warming on a regular basis for the purpose of facilitating the formation of crystals with uniform orientation and regularly

RESULT AND DISCUSSION

Structure and Crystal Size of ZnO thin films

The structure and size of the crystals of ZnO thin films were tested by X-ray diffraction (XRD) . The XRD pattern of ZnO thin films with various concentration of 0.6 M ; 0.7 M and 0.8 M shown in Figure 2a , 2b and 2c and the XRD pattern of ZnO thin films with a variety of post - heating 500^{0}C, 550^{0}C, 600^{0}C and is shown in Figure 3a, 3b and 3c .

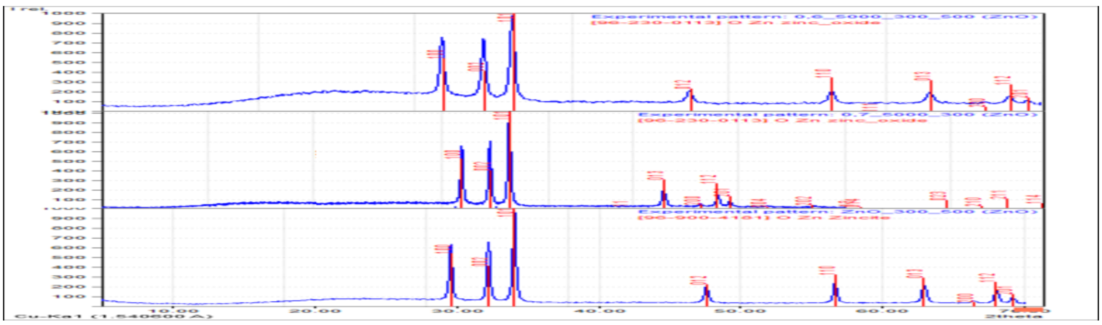


Figure 2. XRD spectrum of ZnO thin films with various concentration

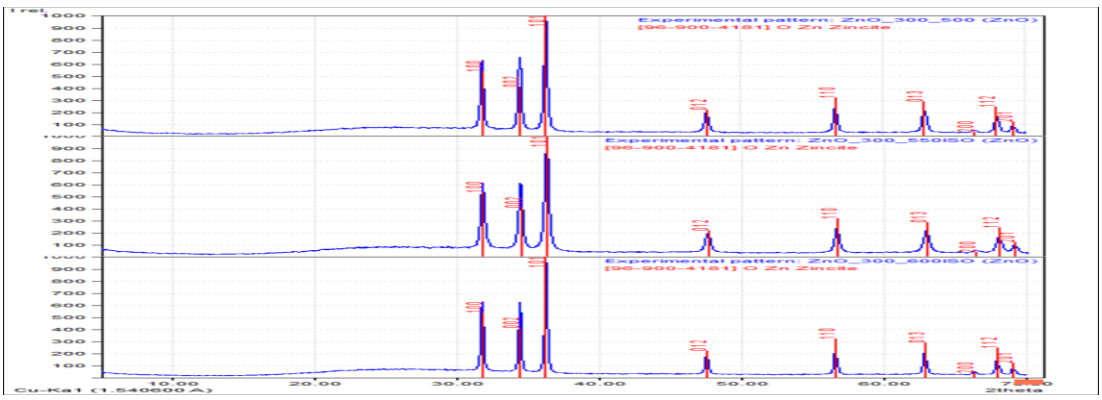


Figure 3. XRD spectrum of the ZnO thin film with the variation of post - heating

XRD patterns of thin films with various concentration (Figure 1) and the variation of post - heating (Figure 2) were synthesized by the method of sol - gel spin - coating were analyzed by using the search march showed that all the peaks of ZnO thin films according to the standard peak of ZnO card JCPDS 80-0075 , it indicates that the ZnO crystals have formed . For all the samples have fields that same crystal plane (100), (002) and (101) and hexagonal -shaped ZnO crystals. The intensity of the peak (chopped) crystal thin film to a concentration of 0.7 M and for the post - heating temperature of 600^0C highest , this is because the energy obtained ZnO atoms of ZnO thin film with a concentration of 0.7 m and post - heating 600^0C to form higher crystal field , so he has a better ability to organize itself in certain fields , meaning that the concentration and post - heating affects the intensity of the XRD terbentuk.Pola crystal thin films with various concentration (Figure 1) and the variation of post- heating (Figure 2) were synthesized by the method of sol - gel spin - coating were analyzed by using the search march showed that all the peaks of ZnO thin films in accordance with the peak of ZnO standard JCPDS card 80-0075 , it indicates that the ZnO crystals have formed . For all the samples have fields that same crystal plane (100) , (002) and (101) and hexagonal -shaped ZnO crystals . The intensity of the peak (chopped) crystal thin film to a concentration of 0.7 M and for the post - heating temperature of 600^0C is highest, this is because the energy obtained ZnO atoms of ZnO thin film with a concentration of 0.7 M and post - heating 600^0C to form higher crystal field , so he has a better ability to organize itself in certain fields, including that the concentration and post - heating affects the intensity of the crystals formed.

The analysis is based on the value of FWHM indicates a change different values for each concentration and post-heating temperature. Looks value of FWHM of ZnO at concentrations of 0.6 M and post-heating temperature of 600^0C has the smallest value respectively 0.24600 and 0.20050. Differences FWHM values indicate the difference in the size of the ZnO crystal due to variations in concentration and post-heating temperature. ZnO crystal size can be calculated using the Scherrer equation (Cuility and Stock, 2001), namely: $D = \frac{0.9\lambda}{\beta \cos\theta}$

(1)

where D is the crystal size , λ is the wavelength , β is the FWHM (full width half maximum), θ is the angle of diffraction and a, c is the lattice parameter, the results are shown in Table 1 for various concentration and Table 2 for variations post- heating

Table 1. The shape and size of the crystal ZnO thin films with various Concentration

Consentration	Phase	Peak		Crystal Size	Cristal Shape
		2θ (degree)	FWHM (degree)	(nm)	
0,6 M	ZnO	36,2663	0,32990	25,4	hexagonal
0,7 M	ZnO	36,2699	0,29130	30,3	hexagonal
0,8 M	ZnO	36,2377	0,24600	34,1	hexagonal

Table 2. The shape and size of the crystal ZnO thin films with a variety of post – heating

Temperature (°C)	Phase	Peak		Crystal zize (nm)	Crystal Shape
		2θ (degree)	FWHM		
500	ZnO	36,2377	0,24600	34,1	hexagonal
550	ZnO	36,2242	0,32190	32,4	hexagonal
600	ZnO	36,2472	0,20050	40,2	hexagonal

Based on tables 1 and 2 shown to differences between the crystal size, which shows that the difference in concentration and post - heating temperature is able to produce different sizes of ZnO crystals. The crystallite size of ZnO thin films least 25.4 nm for a concentration of 0.6 M and the greatest concentration of 34.1 nm to 0.8 M. The crystallite size of ZnO thin films least 32.4 nm for the post - heating temperature of 550°C and most large 40,2 nm for the post - heating temperature of 600°C. This shows that difference affects the concentration and temperature of heating the crystal size of ZnO thin films are formed .

Optical properties of ZnO Thin Films

ZnO thin film samples were synthesized with various concentration and post - heatng later in the characterization by UV - Vis spectrometer to obtain the optical properties of ZnO thin films covering the transmittance , refractive index , thickness and bandgap energy .

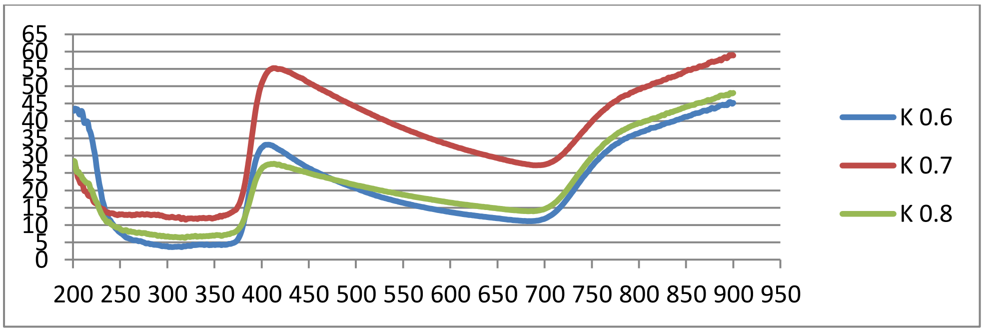


Figure 4. transmittance spectra for samples with various concentration

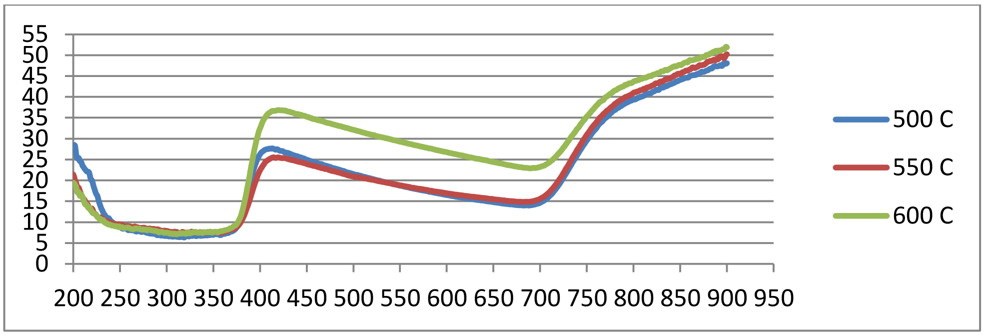


Figure 5. transmittance spectra for samples with variation of post - heating

Based on Figure 4 , ZnO thin films were synthesized with a concentration of 0.6 M , transmitansinya the lowest (45.2 %) in the wavelength range 200 nm - 900 nm. Highest transmittance values occur in ZnO thin films with a concentration of 0.7 M (58.8 %). This relates to the quality of the thin film is formed , both in terms of the crystal structure , grain size and be a reference to get a good quality thin films disintesisi with a concentration of 0.7 M. According to figure 5 , a thin ZnO synthesized by post - heating temperatures 500^{o}C , transmitansinya the lowest (48.0 %) in the wavelength range 200 nm - 900 nm. Highest transmittance values occur in ZnO thin films by post - heating temperature of 600^{o}C (52.0 %) . It is appropriate according to Annie (2010), an increase in transmittance at higher temperatures due to optical scattering caused by compaction and grain growth between particles formed . It is a matter of reference to get a good quality thin films required heating at higher temperatures (600^{o}C)

To calculate the value of the refractive index and thickness of ZnO thin films were synthesized with various concentration and post - heating temperature using equation (H.F. Hussein,et al .2011).

$$n = \frac{(1+R^{1/2})}{(1-R^{1/2})} \qquad (2)$$

where n = refractive index thin films , and R = reactance

Thin layer thickness measuring by optical methods determined by the relationship of refractive index thin film is calculated by equation (Bilalodin , 2012) :

$$d = \frac{\lambda_1.\lambda_2}{2n(\lambda_2 - \lambda_1)} \qquad (3)$$

d is the thickness of thin films and λ1 , λ2 respectively wavelengths that produce the maximum and minimum reactance .

Table 4. The values of the refractive index and thickness of samples with various concentration

Consentration	Refractive index	thickness (nm)
0,6 M	1.74	158
0,7 M	1.59	182
0,8 M	1,74	128

Table 5. The value of the refractive index and thickness of the sample with a variety of post – heating

Post-heating	Indeks bias	Ketebalan (nm)
500°C	1.74	128
550°C	1.75	160
600°C	1,68	140

Based on Table 4 that the refractive index of ZnO thin films to a concentration of 0.6 M , 0.7 M and 0.8 M nearly equal , but the thickness of the smallest to the concentration of 0.8 M. This is due to the concentration of 0.8 M size most large crystal grains and more tightly so that its thickness is diminishing . In Table 5 shows that the smallest thickness of the thin film to a temperature of 500^0C and 550^0 C greatest for temperature. This means that the heating temperature of 500^0 C most large crystal grain size and more tightly so that its thickness is diminishing .

Band gap energy (energy band gap) which is calculated by the method Touc Plot (J. Tauc , 1966) by way of a graph ekstrapolarisasi (hυ) as abscissa and (αhυ) n as the ordinate axis to cut energy in order to obtain the value of the energy band gap optical. The slope of the straight line fitting in Figure 6 is a CD .

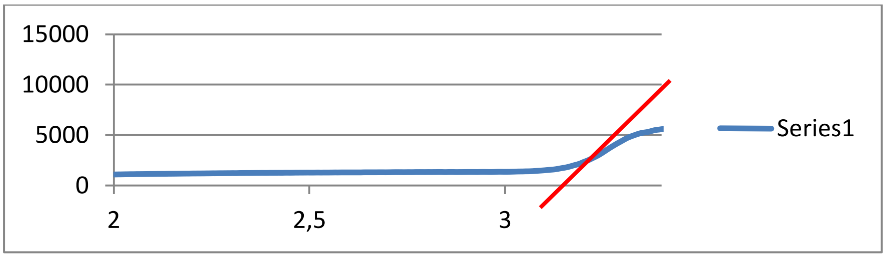


Figure 6. Curve (αhυ) 2 as a function of energy in ZnO thin films with a concentration of 0.6 M

The value of the energy band gap of ZnO thin films with various concentration and post - heating temperature as shown in Table 6 and 7

Table 6. The energy band gap of ZnO thin films for various concentration

Consentration	Enery band gap (eV)
0,6 M	3,15
0,7 M	3,16

0,8 M	3,14

Table 7. The energy band gap thin films ZnO for various Post-heating temperature

Post-heating temperature	Energy Band gap (eV)
500^{o}C	3,14
550^{o}C	3,16
600^{o}C	3,14

Based on table 6, visible value the energy band gap of ZnO thin films ascending with increasing concentration , this indicates that the quality of ZnO thin films at a concentration of 0.6 M better than ZnO thin films at a concentration of 0.7 M and 0.8 M. Under the Table 7 looks values of energy band gap of ZnO thin films decreased with increasing heating temperature. This suggests that the quality of ZnO thin films at a temperature of 600^{o}C better than ZnO thin films at temperatures of 500^{o}C and 550^{o}C. Band gap energy show movement of electrons in the material across the valence band to the conduction band . Energy band gap associated with the concentration and temperature of the post – heating.

CONCLUSIONS

ZnO thin films have been successfully synthesized by the method of sol - gel spin- coating on a glass substrate. Most small crystal size of 25.4 nm for a concentration of 0.6 M and the greatest concentration of 34.1 nm to 0.8 M. In the post - heating temperature of 550^{0}C smallest size of ZnO crystals 32.4 nm and 40.2 nm greatest post - heating to 600^{0}C. ZnO thin films were synthesized with a concentration of 0.6 M , transmitansinya the lowest (45.2 %) with the energy band gap of 3.15 eV in the wavelength range 200 nm - 900 nm. Highest transmittance values occur in ZnO thin films with a concentration of 0.7 M (58.8 %) with the energy band gap of 3.16 eV . ZnO thin films were synthesized by post - heating temperature of 500^{0}C, transmitansinya the lowest (48.0 %) with the energy band gap of 3.14 eV in the wavelength range 200 nm - 900 nm and a transmittance value is highest in ZnO thin films with temperature post - heating 600^{0}C (52.0 %) with the energy band gap of 3.14 eV .

REFERENCES

Annisa Aprilla, Herman Bahar, Rahmat Hidayat. (2010) Preparasi Lapisan Tipis ZnO Transparan menggunakan Metode Sol-Gel beserta Karakterisasi Sifat Optiknya. Prosiding Seminar Nasional Fisika

Changzheng. Z, (2009). Effect of the oxygen pressure on the microstructure and optical properties of ZnO film prepared by laser moleculer beam epitaxy. Elsevier Physics B 404

Cheng, X.L, (2004). ZnO nano particulate thin film: preparation, characterization and gas sensing property. Elsevier Sensor and Actuators, Vol 102

Cullity B.D and Stoc. S.R, (2001). Elemente of X-Ray of diffractions, Prentice Hall.

Cao, Guozhong, (2004). Nanostructurs dan Nanomaterial. Imperial College Press. USA

C. R. Vestal, Z. J. Chang, (2004). Int. J. Nanobiotechnology. Vol 1. Nos $^1/_2$.

C.T.Chen, C.L. Cheng, T.T. Chen, Y.F. Chen, (2009). Improved physical properties of ZnO nanostructures by inclusim. Material Letters 537-

D. Sridevi dan K.V. Rajendran, (2009), Synthesis And Optical Characteristics Of ZnO Nanocrystals, Bull Mater Sci, Vol 32. Indian Academy Of Sciences.

Guanglong. Z, (2007), Orientation enhancement of polycrystalline ZnO thin film through thermal. Elsevier Materials Letters . Vol 61.

George. A. (2010). Microstructurure and field emission characteristics of ZnO nanoneedles grown by physical vapor deposition. Elsevier Materials Chemistry and Physics Vol 123.

Heidari.A. dan Younesi. H. (2009). Controllables Systhesis Of Flower-Like ZnO Nanostructure With Hydrothermal Method. University, Noor, Iran

H.F. Hussein, Ghufran Mohammad Shabeeb dan S.Sh. Hashim. (2011). Preparation ZnO Thin Film by using Sol-gel processed and determination of thickness and study optical properties. J. Master. Environ. Sci. 2 (4).

Jing .S.H dan Ching , (2008). Influences of ZnO solgel thin film, Influences of ZnO solgel temperature using all solutions based processing. Jurnal of App Physcis

Liou Xiao-bo, Shen Hong-Lie, Zhang Hui, Li Bin-bin, (2007). Optical properties of nano sized ZnO Flims prepared by Sol-gel process. T.N. Metals Society of cina.

Matsuda (1988), "Amorphous Silicon From Glow Discharge Plasma", *Procedings International Workhop on physics of Materials,* Jakarta, 250-255.

Milton Ohring (1992). The Materials Science of Thin Films. Academic Press Inc. Harcout Brace Jovanovich, publishers, Boston.

Muhamad Adi, K. Sofjan Firdaus, Whayu Setia Budi, (2007). Efek Magneto Optis pada lapisan tipis (ZnO). Berkala Fisika Vol 10. No. 1. hal 31-34

Omar.M.A. (1975). Elementary of Solid State Phisics. Adison Wesley

S.Ilican. dkk (2008). Preparation and Characterization of ZnO Thin Films Deposited By Sol-gel Spin Coating Method. Journal of Opto and advanced Materials Vol 10.

Sumetha Suwanboon, Ratana Tanattha dan Ratana Tanakorn, (2008). Fabrication And Properties Of Nanocrystalline Zinc Oxide Thin Film Prepared By Sol-gel Method. Songklanakarin journal of Science and technology. 30(1), 65-69

Tamiko.O, Tomoaki. I , Kenji. E. , Jes .A. , Rajk, Thareja, (2003)., Synthesis of P-type ZnO thin Films using co-doping techniques based on KrF excimer laser deposition. Thin Solid Films 435. 49-55

Ziaul Rizal Khan, Mohd Shoeb Khan, Mohammad Zulfequar, Mohd Shahid Khan. (2011). Optical And Structural Properties Of ZnO Thin Films Fabricated by Sol-gel Methods. Materials Sciences Aplication.