PREPARATION OF INDIUM TIN OXIDE (ITO) THIN FILMS BY SOL-GEL METHOD: THE EFFECT OF COATING SPEED ON STRUCTURAL AND OPTICAL PROPERTIES

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NOR SARAHTUL NADIRAH BINTI HAIROL NIZAN

Thesis submitted in fulfillment of the requirements
for the award of the degree of
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DECEMBER 2016

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DEDICATION

I dedicate this thesis to my beloved family, supervisor, and friends for their love, encouragement and prays along my journey.

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ABSTRACT

The transparent conducting indium tin oxide (ITO) thin films were prepared by sol-gel and spin coating technique at various coating speed (500, 1500 and 3000 rpm). ITO thin films containing 8% Sn by weight were successfully prepared by heat treatment at 500℃ in this study. The structural and optical properties significantly depend on the coating speed. From the XRD result obtained, the prepared ITO thin film has cubic structure, and (222) is its preferred plane. As the coating speed increase, films shows a lower degree of polycrystallinity. The grain size in the range nanometer decreased with increasing coating speed. The transmittance value of all ITO thin films are more than 90%. The band gap are calculated from plotting product of adsorption coeeficients in photon energy $(\alpha h v^2)$ against photon energy (*hv*) is in the range of 4.18 eV to 4.28 eV. The PL spectra decreases, as the coating speed increased.

ABSTRAK

Lutsinar indium timah oksida (ITO) filem nipis telah disediakan mealui kaedah sol-gel dan teknik lapisan putaran di salutan pelbagai kelajuan (500, 1500 dan 3000 rpm). ITO filem nipis yang mengandungi 8% timah mengikut berat telah berjaya disediakan oleh rawatan haba pada 500℃ dalam kajian ini. Sifat-sifat struktur dan optik adalah ketara bergantung kepada kelajuan putaran lapisan. Dari hasil XRD yang diperolehi, ITO filem nipis yang disediakan mempunyai struktur padu, dan (222) adalah orientasi pilihan. Apabila berlaku peningkatan kelajuan lapisan, filem menunjukkan darjah yang lebih rendah poli kristal. Saiz butiran dalam julat nanometer menurun dengan peningkatan kelajuan salutan putaran. Nilai pemindahan semua filem nipis ITO lebih daripada 90%. Jurang jalur dikira daripada plot produk pekali penjerapan dalam tenaga foton $(\alpha h\nu)^2$ terhadap tenaga foton ($h\nu$) adalah dalam lingkungan 4.18 eV kepada 4.28 eV. PL spektrum berkurangan apabila kelajuan putaran salutan menaik.

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LIST OF SYMBOLS

~	-	approximately
%	-	percent
λ	-	wavelength
nm	-	nanometer (10^{-9})
η	-	coulombic efficiency
2θ	-	Bragg angle
^{o}C	-	degree celcius
Å	-	angstrom (10^{-10})
h	-	hour
s	-	seconds
t	-	time
rpm	-	rotation per minute

LIST OF ABBREVIATIONS

ARE	-	activated reactive evaporation process
AZO	-	aluminium zinc oxide
BCC	-	body centered cubic
CTE	-	coefficient of thermal expansion
FESEM	-	field emission scanning electron microscopy
ITO	-	indium tin oxide
NBE	-	near band edge
NIR	-	near infrared
NSP	-	nebulizer spray pyrolysis
OLED	-	organic light-emitting diode
PDF	-	powder diffraction file
PET	-	polyethylene terephthalate
PL	-	photoluminescence
RF	-	radio freuency
UV VIS	-	ultraviolet and visible
XRD	-	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THE PROBLEM

Transparent conducting oxides (TCOs) have two physical properties which are high optical transparency and high electrical conductivity (C.H. Yang). These two physical properties make them as special semiconductors. S. Elmas et al, (2013) mentioned that among numerous transparent conducting oxide (TCO) films, Indium Tin Oxide (ITO) thin films is n-type and highly degenerate. It has wide band gap which is of more than 3.4 eV. It has wide applications in optoelectronic devices such as liquid crystal displays and solar cells (R.G. Gordon, 2000)

However, A Weiser et al., (2015) stated that the price of indium has fluctuated markedly due to the recent growth of these industries, because the element is relatively scarce in the earth's crust. ITO is more costly than aluminium zinc oxide (AZO). Even though, AZO has become a TCO due to cheaper in price and generally good optical transmission performance especially in the solar spectrum. ITO offers better electrical conductivity (Melvin David Kumara et al., 2015). Due to this matter, the alternative way to lower cost methods of preparing ITO will be investigated throughout this study.

There are many ways to prepare ITO thin films. S. Li et al., (2006) mentioned that sol–gel method is the most preferable wet chemical processes to synthesis ITO thin film. It has numerous benefits which the controllable composition of ITO thin films and low cost. This is because vacuum or expensive devices are not needed to carry out sol-gel method. Other than that, substrates that may vary considerably in shape can be coated simply with a solution by dip, spin or spray coating. High-quality ITO coatings can be produced effectively with this method (L. K″orösia et al., 2014).

Based on W.S. Lau et al., (1986), highly transparent and conducting undoped indium oxide thin films shows a resistivity of $\sim 4 \text{ x } 10^{-4}$ Ω-cm, a carrier density of $\sim 9 \text{ x } 10^{20} \text{cm}^{-3}$ and a mobility of ~18 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ at a substrate temperature more than 70 °C and a deposition rate of ~8 Å/s by an activated reactive evaporation process (ARE). From the findings, optical band gap of ITO films is about 3.3 eV, which is lower than that of a high temperature deposited tin doped indium oxide film.

It is found that undoped indium oxide films with the best conductivity cannot be obtained if a threshold temperature of ~200 °C is exceeded either during deposition or after deposition vacuum anneals. Highly conductive tin doped indium oxide can be easily obtained at high temperature of ~400 °C by ARE.

1.2 STATEMENT OF THE PROBLEM

The properties of ITO thin film will be affected if they have different thickness. (Ghoranneviss et al., 2015). According to literature review, ITO films prepared using sol-gel method and effect of coating speed have gained less attention, which gave us the motivation to carry out this study. Herein, the dependence of the structural and optical properties of sol-gel ITO thin films on the various coating speed are going to investigate.

1.3 OBJECTIVES OF THE STUDY

The objectives of this study are:

1. To synthesis thin film of ITO deposited on a glass substrate by sol-gel method with spin coating.

2. To study on how the different coating speed gives effect on its structural characteristics using X-Ray diffraction (XRD) and Field Emission Scanning Electron Microscopy (FESEM).

3. To investigate the effect of different coating speed on the optical properties of ITO thin film using UV-Vis spectrocopy and Photoluminescence (PL) Spectrometry.

1.4 SCOPE OF THE STUDY

The aim of this study is to elucidate the crystallization quality of ITO thin films which is prepared by sol-gel method. These structural and optical properties of ITO thin films were synthetically characterized using XRD and FESEM. Apart from that, the grain size, the transmittance of ITO thin films and band gap are investigated using UV-Visible spectroscopy and PL spectrometry. The attention of this study is focused on effect of different coating speed on structural and optical properties.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter will discussed the overview of the fabrication process and the characterization studies of ITO thin films concerning the crystalline structure, the degree of polycrystallinity, the grain size, optical transmission and energy band gap.

2.2 FABRICATION PROCESS

There are many types of fabrication process to synthesis ITO thin film. To name, they are magnetron sputtering, sol–gel process, pulsed laser and chemical vapor deposition, spray pyrolysis, and nebulizer spray pyrolysis (NSP). All of these methods have their own advantages and disadvantages (M. Thirumoorthia et al, 2016). There is a lot of thing that should be considered before deciding which technique is the most suitable method. For this work, ITO thin film is synthesized using sol-gel technique.

2.2.1 Sol Gel Technique

John D. Wright et al said that sol-gel processing involving the generation of colloidal suspensions (“sols”) which are subsequently converted to viscous gels and to solid materials. This controlled method has many advantages, which led to its historical use before the underlying scientific principles were understood. In recent years increased understanding of these principles has led to a great increase of interest in the method, and to its application in the production of a wide variety of advanced materials.

A few stages are included in the sol–gel process for getting a gel, to be specific; mixing, gelation, aging, drying, and sintering.

Ramalingam,(2014) mentioned that sol-gel technique gives benefits as it can create a thin bond-coating to give superb adhesion between the metallic substrate and the top coat. Next, it can produce thick coating to give corrosion protection performance. Besides that, using this technique we can easily shape materials into complex geometries in a gel state. It can have low temperature sintering ability, commonly from 200 °C and up to 600 °C.

ITO thin films prepared by sol-gel method show a relatively high resistance. The wide usage of ITO thin films using sol-gel is difficult to acquire metal alkoxides as raw materials for their unavailability and high cost. (LI Zhi-hua et al., 2008)

2.2.2 Deposition Method (Spin Coating on Glass Substrate)

Glass has numerous properties that make it a perfect substrate for interposers which are low dielectric constant, ultra-high resistivity and low electrical loss, and adjustable coefficient of thermal expansion (CTE) (Shorey, 2014). Besides glass, there are a lot of other materials that can be used as a substrate such as polyethylene terephthalate (PET), quartz and silicon wafer. For this study, glass substrate is used as a substrate.

Spin coating, which is a typical spin process consists of a dispense step where the resin fluid is deposited onto the surface of substrate. Then, a high speed spin step to make the fluid thin and a drying step to eliminate excess solvents from the film produced. The schematic of spin-coating process is shown in Figure 2.1. In general, higher spin speeds and longer spin times produce thinner films.

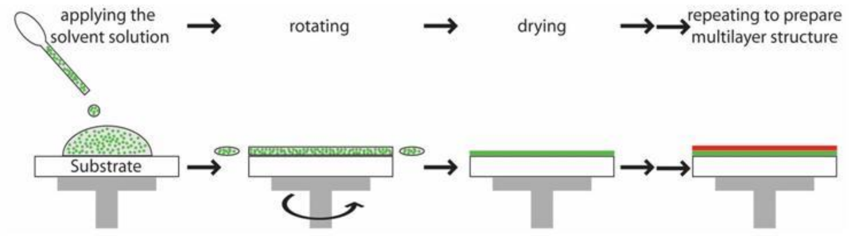


Figure 2.1. Schematic of the spin-coating process.

Source: Reproduced from (Sohrab Ahmadi Kandjani et al., 2015)

2.3 FUNDAMENTAL PROPERTIES OF ITO THIN FILM

The fundamental properties of the ITO thin films are discussed. These films were deposited at various coating speed (rpm) of thin film.

2.3.1 Structural Properties

Based on studies carried out by Landolt,(1975), indium oxide crystallizes in two different structures which are body centered cubic (BCC) and hexagonal as shown in Figure 2.2. It is complex structures as it consists of 16 molecules, that is 80 atoms. Tin oxide (SnO_2) single crystal has tetragonal rutile structure and have two formula units per unit cell. The unit cell contains six atoms which are two tin and four oxygen. The structure of ITO crystallized in BCC and hexagonal structures.

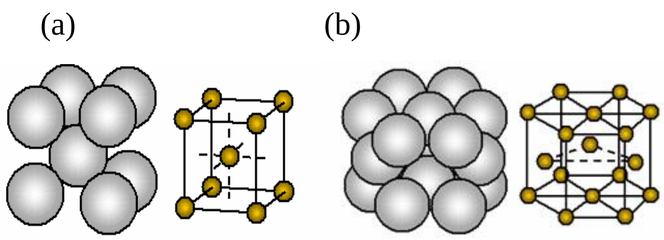


Figure 2.2. Crystalline structure of a) BCC and b) hexagonal close packed.

Source: Reproduced from (astarmathsandphysics.com)

The crystallographic properties and the average grain size were studied by XRD and FESEM. Giusti,(2011) stated that film orientation changed as the speed of spin coating increased which give meaning that less film thickness obtained. The (222) preferred orientation observed up to 5000 rpm was increasingly changed to (521) orientation as shown in Figure 2.3. The film tended to become more polycrystalline. From the study, it can be said that when film thickness increase, films tended to show a higher degree of polycrystallinity.

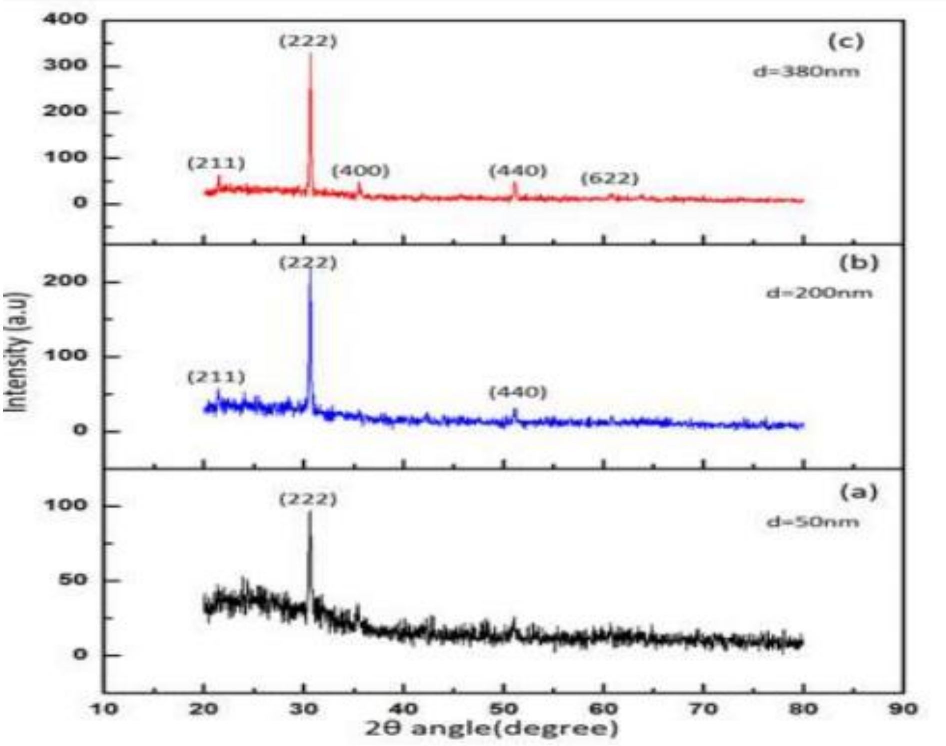


Figure 2.3. XRD pattern of ITO films with different thickness.
Source: Reproduced from (Forat H. Alsultany et al., 2014)

From table 2.1, recent study has shown that the grain size increased from 31.77 nm to 41.82 nm with increasing film thickness. While Figure 2.4 shows the FESEM images of the ITO thin films. The grain sizes increased with increasing film thickness (Forat H. Alsultany et al., 2014).

Table 2.1

The grain size increased with increasing film thickness

Source: Reproduced from (Forat H. Alsultany et al., 2014)

Film thickness (nm)	**Grain size (nm)**	**rms roughness (nm)**	**Resistivity (Ω -cm)**	**Energy gap (eV)**
50	31.77	1.71	$4.5 \text{ X } 10^{-3}$	3.80
100	34.32	2.54	$9.7 \text{ X } 10^{-4}$	3.75
380	42.82	4.81	$3.8 \text{ X } 10^{-4}$	3.44

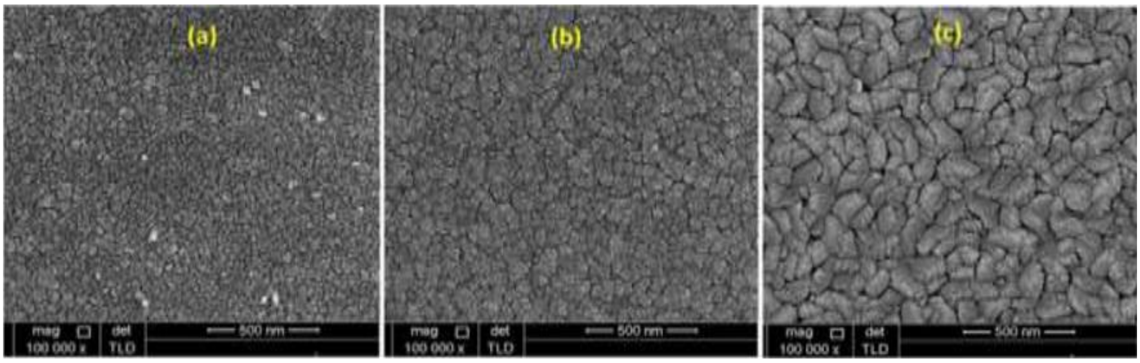


Figure 2.4. FESEM of (a) 50 nm, (b) 200 nm, and (c) 380 nm thick ITO films.

Source: Reproduced from (Forat H. Alsultany et al., 2014)

2.3.2 Optical Properties

Based on our findings, the optical properties of ITO thin films were studied using an UV–Visible Spectrometer. In the UV region, indium oxide and ITO thin films show high ultraviolet absorption because the fundamental direct band gap is about 3.5 eV and the absorption is related to inter-band transitions. (J.-C. Manifacier et al., 1977), it is found to lie between 3.5 and 4.1 eV.

Based on Du, et al.(2014), ITO thin films has attractive properties including high level of transmittance in the visible region as well as electrical conductivity that is unique. This is mainly due to ITO's highly degenerate behavior as an n-type semiconductor with a large band gap of around 3.5 to 4.3 eV.

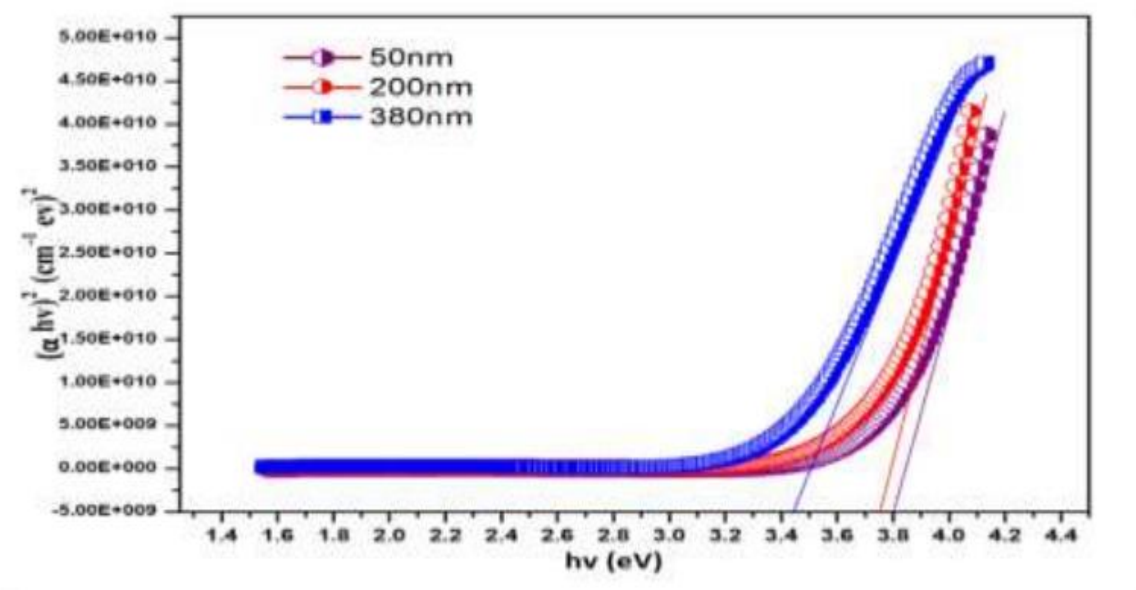


Figure 2.5. Variations in the optical band gap of the ITO thin films
Source: Reproduced from (Forat H. Alsultany et al., 2014)

Figure 2.5 above shows the energy band gaps of ITO thin films. Based on the findings, the energy gaps of ITO thin films have been calculated from the plot of $(ahv)^2$ versus hv. While, the absorption coefficients (α) were calculated from the optical transmission (T) using the equation as follows:

$$\alpha = (\frac{\ln 1}{T}) / D \tag{2.1}$$

where D is thickness of thin films. The photon energy (hv) values were calculated using the equation below:

$$hv = 1240/\lambda \tag{2.2}$$

where λ is the wavelength of the thin film (L. Kerkache et al., 2010). It is found that the average energy gap decreased when film thickness increased. In other words, slow coating speed produce small energy gap. The highest value of the energy gap (3.80 eV) is observed for 50 nm thick thin film.

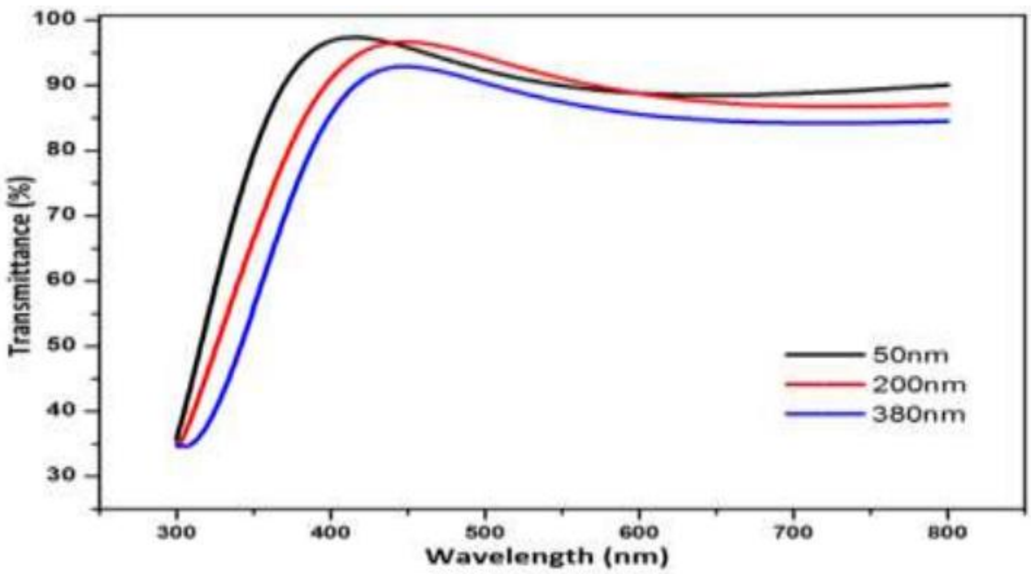


Figure 2.6. Optical transmission spectra of the ITO thin films.
Source: Repoduced from (Forat H. Alsultany et al., 2014)

The optical transmission of ITO thin films for 300 nm to 800 nm wavelength range is shown in Figure 2.6 above. The findings stated that the optical transmission of ITO thin films decreased as film thickness increased.

CHAPTER 3

MATERIALS AND METHODS

3.1 INTRODUCTION

The preparation of ITO thin films using sol-gel method, deposition method by spin coating and the characterization of ITO by XRD, FESEM, UV-Vis spectroscopy, and PL spectrometry are explained. A glass substrate is used as a substrate and the annealing temperature is kept at 500 °C for 1 hour. The limitation of this study is the different coating speed used to deposit ITO on glass substrates which undergoes spin coating at speed of 500, 1500, and 3000 rpm for 10 seconds for each samples.

3.2 FLOW CHART

The research methodology for this study follows the flow chart shown in Figure 3.1.

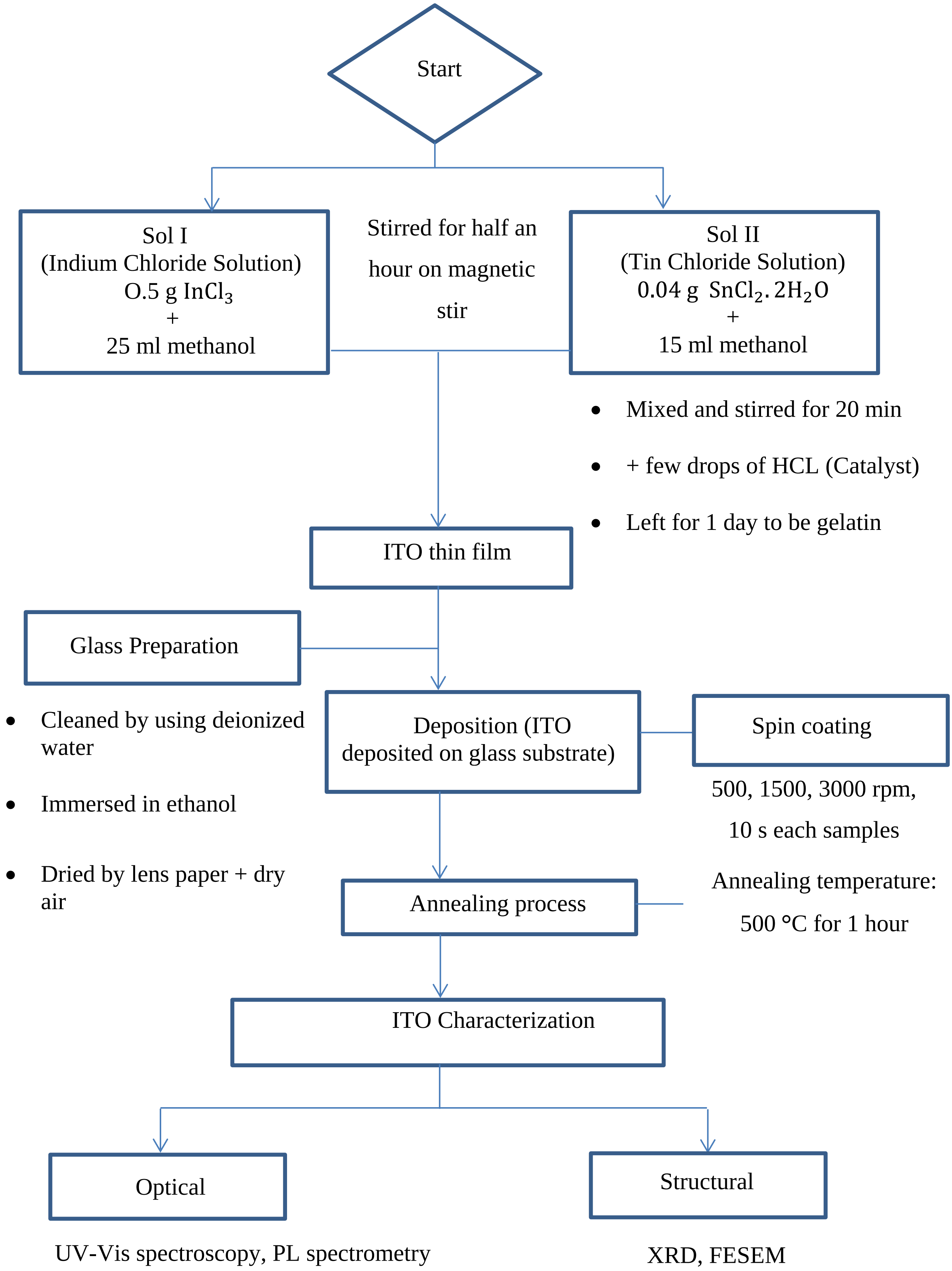


Figure 3.1. Flowchart above is the laboratory experimental work for conducting this study

3.3 ITO SOL-GEL METHOD

For this study, sol-gel technique is used to synthesis the ITO thin film. Firstly, Indium chloride solution (sol I) are prepared by dissolving 0.5 g of $\mathrm{InCl_3}$; molecular weight 221.18 g/mole in 25 ml of methanol. Then, the solution was stirred for half hour on magnetic stir. The second solution was the tin chloride solution (Sol II). $\mathrm{SnCl_2.2H_2O}$; molecular weight 225.6 g/mole is used as a dopant solution depending on the weight of the tin chloride in 15 ml of methanol where the doping ratio of the tin with Indium was took from the following equation $\frac{\mathrm{Sn}}{\mathrm{Sn+In}}$ (8)%. After that, the solution was stirred for half hour on magnetic stir, added gradually to the Sol I. The mix solution was stirred again for at least 20 minutes and a few drops of hydrochloric acid are added as a catalyst. Finally, this solution called ITO solution. The solution is left for one day to be gelation.

3.4 DEPOSITION OF ITO ON GLASS SUBSTRATE (SPIN COATING METHOD)

Then, the process of deposition the precursor solution on the glass substrate is carried out using spin coating method. ITO thin film was annealed for one hour at 500 °C in a furnace. In this work, a dimension (30x30x1) mm of microscopic glass slides is used as a substrate. The substrate is cleaned thoroughly before deposition. The substrate is cleaned with deionized water and then immersed them in the ethanol. Finally, the substrates are dried by lens paper and dry air.

Figure 3.2. Spin coater

Spin coater is used to deposit the ITO on glass substrate. For this study, the coating speeds are varied to produce different thickness of thin film. 500 rpm, 1500 rpm, and 3000 rpm are used. This process took about 10 seconds for each sample. The standard of procedure for spin coating is explained by using flow chart as shown in Figure 3.3.

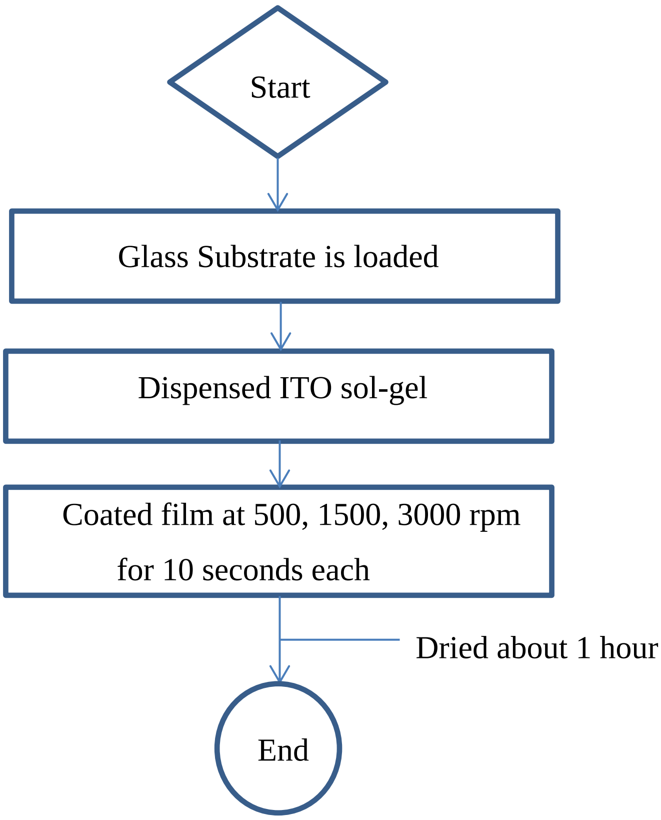


Figure 3.3. Spin coater procedures flow chart

3.5 CHARACTERIZATION OF ITO THIN FILMS

In order to characterize ITO thin film, there are several instruments that have been used to study the properties of ITO thin film which are by XRD, FESEM, UV-Vis spectroscopy, and PL spectrometry. XRD and FESEM are used to characterize the structural properties of ITO thin film. While UV-Vis spectrocopy and PL spectrometry are to study the optical properties of ITO thin film.

3.5.1 X-ray diffraction

A diffractometer can be utilized to make a diffraction pattern of any crystalline solid. With a diffraction pattern, we can identify an unknown mineral, or characterize the atomic-scale structure of a mineral that has been identified. Results are acquired in the form of peak intensity vs. 2θ. Hence, the orientation of crystals can be obtained and intensity of peak shows the film crystallinity.

X-ray diffractometer (D8 ADVANCE with DAVINCI design) using Cu Kα with 1.5418 Å. At a scan rate of 1° /min, samples were scanned from 10 ° - 80 °. The voltage and the current were fixed at 40 kV and 40 mA throughout the analysis.

3.5.2 Field emission scanning electron microscopy

FESEM is a powerful instrument for analyzing topographic at nano-scale levels. It uses windows XP-based computerized operating system with high-resolution digital processing capacity. FESEM is used to study the surface morphologies of ITO thin films produced.

JSM-7800F Extreme-resolution Analytical Field Emission SEM (Figure 3.4 (a)) that has been used in this research provides images at very high magnification and resolution (1.3 nm @ 30 kV). For this study, the range of magnification are 10 000 X to 50 000 X. From the image result obtained, the grain size is compared for each sample. The samples are deposited with platinum to get very clear image (Figure 3.4 (b)).

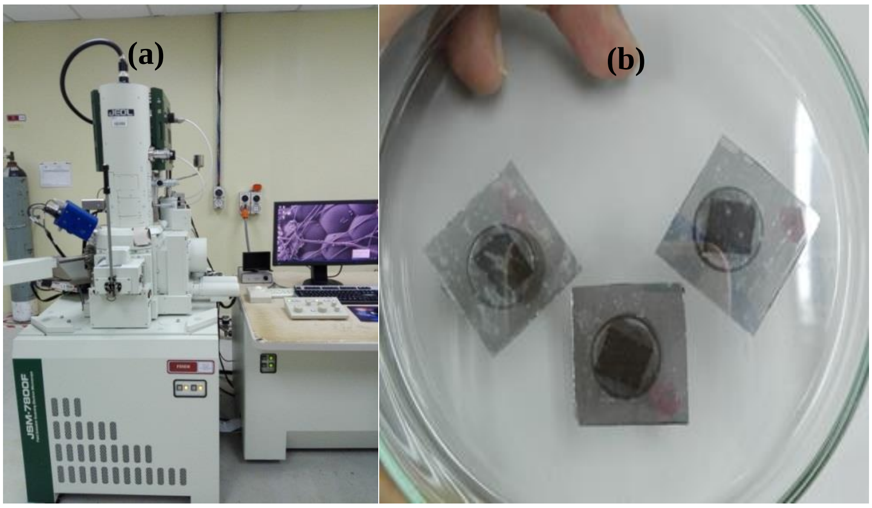


Figure 3.4. a) JSM-7800F Extreme-resolution Analytical Field Emission SEM and b) Samples deposited with platinum

3.5.3 UV-visible spectrocopy

Ultraviolet and visible (UV-Vis) spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Ultraviolet absorption spectra arise from transition of electron with in a molecule from a lower level to a higher level.

UV-Vis (UV – 2600 Shimadzu) in the wavelength range from 200 nm to 800 nm is used to study the optical properties. It produced the result of absorbance and the transmittance of ITO films produced. From the absorbance obtained, the band gap is determined using Tauc’s plot.

Figure 3.5. UV – 2600 Shimadzu

3.5.4 Photoluminescence (PL) spectrometry

Photoluminescence is a process in which a substance absorbs electromagnetic radiation in the form of photons and then re-radiates photons. Quantum mechanically can be explained as an excitation to higher energy state and then return to lower energy state accompanied by the emission of a photon. PL spectrometry is used to study the optical properties in term of the energy band gap.

Edinburgh Instrument NIR 300/1 is used for this characterization. The wavelength range is from 200nm to 900nm. The filter used is 455 nm.

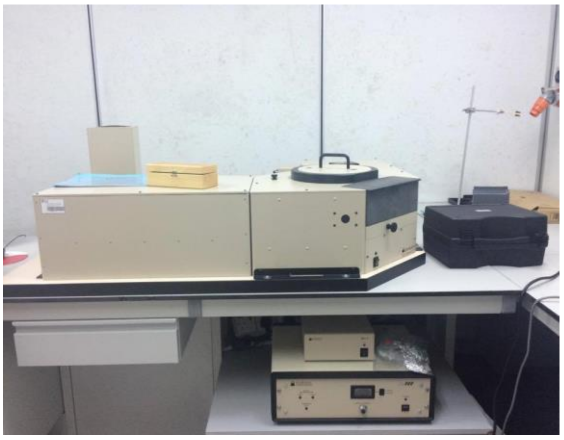


Figure 3.6. Edinburgh Instrument NIR 300/1

CHAPTER 4

RESULT AND DISCUSSION

4.1 INTRODUCTION

In this chapter, the results obtained from XRD, FESEM, UV-VIS spectrocopy and PL spectrometry analysis were discuss. The discussion will be consisted of plotted graph, images and tabulation of data.

4.2 SYNTHESIS OF ITO SOL-GEL

Figure 4.1 shows the sample of synthesized ITO sol-gel after left for 1 day to be gelatin. These sol-gel are then be deposited on glass substrates using spin coating method with different speed of coating which are 500, 1500 and 3000 rpm at 10 seconds for each substrates. After spin coating, the samples are annealed in a furnace at temperature of 500 °C for one hour. From the observation, ITO sol-gel is colorless and has a bit of odor**.**

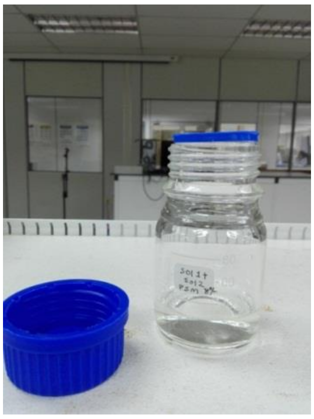


Figure 4.1. ITO sol-gel solution after left to be gelatin for 1 day.

4.3 X-RAY DIFFRACTION ANALYSIS

X-ray diffraction patterns are used to study the crystal structure of prepared ITO thin films. Figure 4.2 shows the XRD pattern obtained for ITO with different speed of coating in 2θ range 20 degree to 80 degree. Reflected X-ray intensity depends on the penetration depth of X-ray(M Benoy, 2009). The diffraction peaks are indexed according to the powder diffraction file (PDF Card - 01-089-4598) as shown in the Figure 4.2.

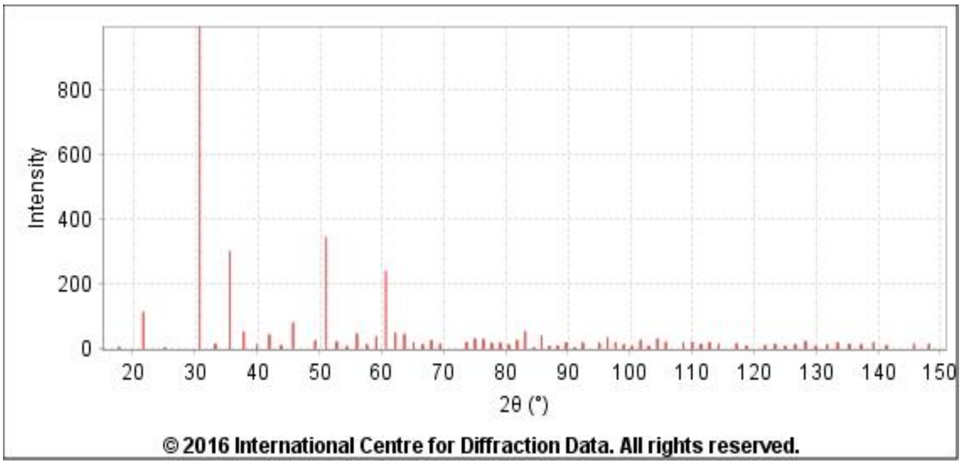


Figure 4.2. The diffraction peaks indexed according to PDF Card - 01-089-4598.

The X-ray diffraction patterns of ITO thin films deposited on glass substrates with different coating speed are depicted in Figure 4.3, 4.4 and 4.5. The diffraction peaks of ITO (2 2 2) appear in all XRD patterns. It can be seen that all the films are polycrystalline in nature and crystallize in a cubic structure with predominant (222) peak. The overall feature of this figure is that all the deposited films are crystalline. None of the spectra detected any characteristic peaks of Sn, SnO, or SnO_2, which means that the tin atoms were doped substitutionally in the In_2O_3 lattice. Furthermore, the relatively low intensity and the markedly broad diffraction peaks indicate that the films are composed of nanoparticles. (M.M. El-Nahassa, 2012). With decreasing coating speed, the intensity of the diffraction peaks increases and new diffraction peaks are detected implying the improvement of crystallinity for these films. This results are correlated with previous study.

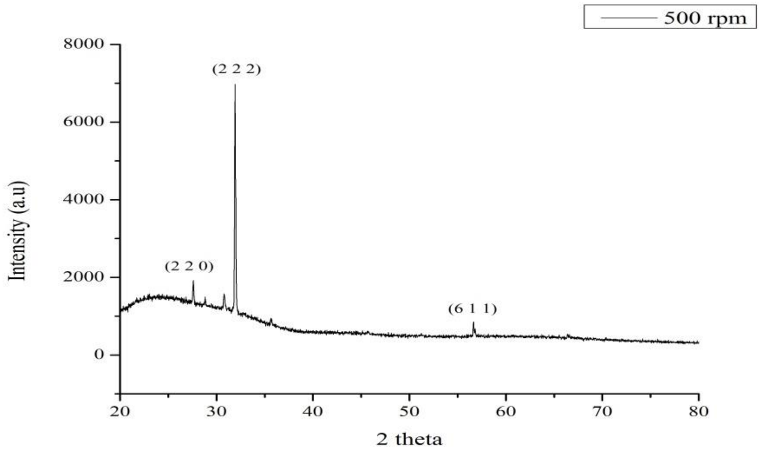


Figure 4.3. XRD pattern of ITO thin film at coating speed 500 rpm.

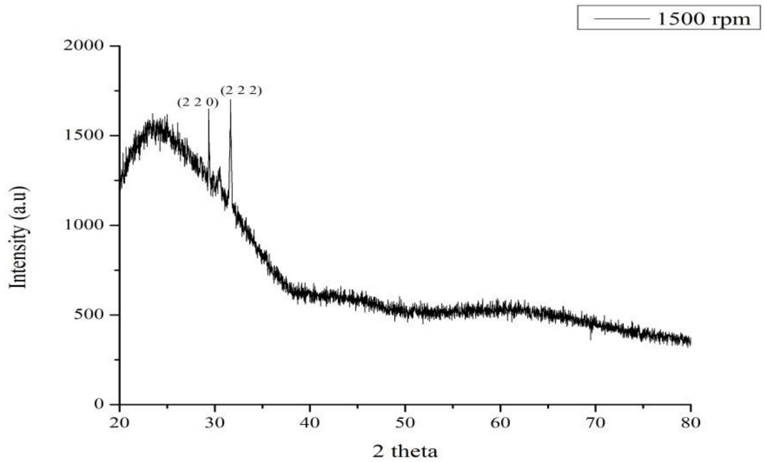


Figure 4.4. XRD pattern of ITO thin film at coating speed 1500 rpm.

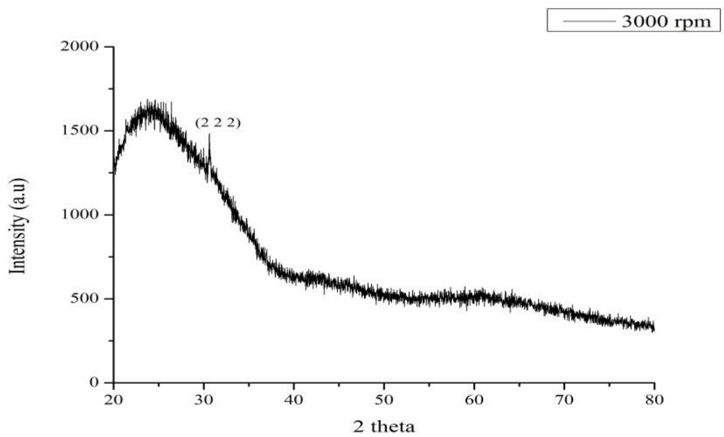


Figure 4.5. XRD pattern of ITO thin film at coating speed 3000 rpm.

Figure 4.3 shows the XRD pattern for the film with coating speed of 500 rpm, in which three major peaks are found and reflections from (220), (222), and (611) planes, with relative intensities of 26.48, 30.54, and 55.89, respectively. Figure 4.4 shows the XRD pattern of the film with coating speed of 1500 rpm, in which two major peak are found with reflections from (220) and (222) planes with relative intensities of 28.48 and 30.54, respectively, in the standard XRD data. Figure 4.5 shows the XRD pattern of the film with coating speed of 3000 rpm, in which one major peak is found and one reflection from (222) plane with 30.54 intensity in the standard XRD data. For the ITO thin film of coating speed 3000 rpm, we obtained only (222) plane at high intensity in the standard data, which is significantly small compared with those thin films at lower coating speed. The absence of reflection from (220) and (611) planes in the 3000 rpm is not due to the orientation but to the sample thickness (A. Pokaipisit, 2008).

The interlayer spacing and crystallite size of ITO thin films are calculates using the most intense peak (222) as tabulate in Table 4.1. Crystallite sizes (*t*) of all the samples were calculated from their respective XRD pattern using the equation as follows:

$$t = \frac{0.9\,\lambda}{\beta \cos\theta} \tag{4.1}$$

Meanwhile, the interlayer spacing (*d*) of the samples were calculated using equation below:

$$n\lambda = 2d \sin\theta \tag{4.2}$$

Where λ is the X-Ray wavelength which is 1.54 Å, θ is Bragg angle, β is the full width at half maximum. By inserting the value as tabulated in Table 4.1 in Equation 4.1 and 4.2, the value of crystal size and interlayer spacing of ITO thin film are shown in Table 4.2.

Table 4.1

Bragg's angle, FHMW and phase name of ITO thin films with different coating speed.

Coating speed (rpm)	**2θ (degree)**	**FHMW (degree)**	**Phase name**
500	30.542	0.033	Cubic
1500	30.542	0.040	Cubic
3000	30.542	0.045	Cubic

Table 4.2

Calculated crystallite size (t) and interlayer spacing (d) for ITO thin films with different coating speed.

Coating speed (rpm)	**Crystallite size, *t* (Å)**	**Interlayer Spacing, *d* (Å)**
500	43.54	2.92
1500	35.92	2.92
3000	31.98	2.92

From Table 4.2, the calculated crystallite size of ITO thin films at coating speed from 500, 1500 and 3000 rpm is 43.54 Å, 35.92 Å and 31.98 Å respectively. It is seen that the crystallite size decreases with the increase of coating speed. With decreasing coating speed, the surface energy decreases. As the surface energy decreases, surface mobility of the species and grain boundary migration increases resulting in lower strain and enhancement in crystalline grain sizes. (M.M. El-Nahassa, 2012). While the value interlayer spacing of all ITO thin films prepared are the same which is 2.92 Å.

4.4 FESEM ANALYSIS

The surface morphologies of ITO thin films with dopant concentration of 8 wt% Sn and different speed coating of 500, 1500 and 3000 rpm were investigated using FESEM at different magnification are shown in Figure 4.6, 4.7, and 4.8. The magnification of FESEM are in range from 10 000 X, 20 000 X and 50 000 X respectively. The average grain sizes for each of ITO thin films were observed**.**

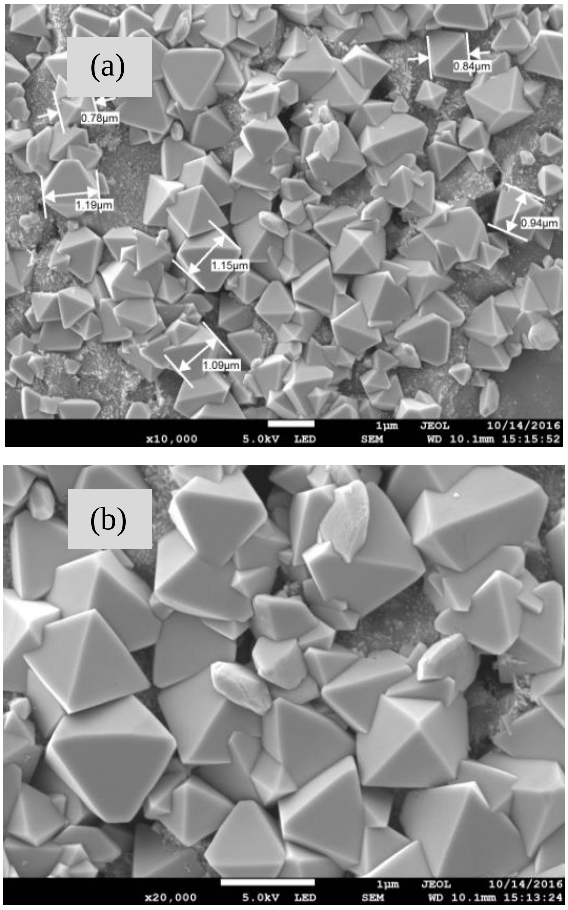


Figure 4.6. FESEM images ITO thin film at coating speed 500 rpm at magnification of (a) 10 000 X and (b) 20 000 X

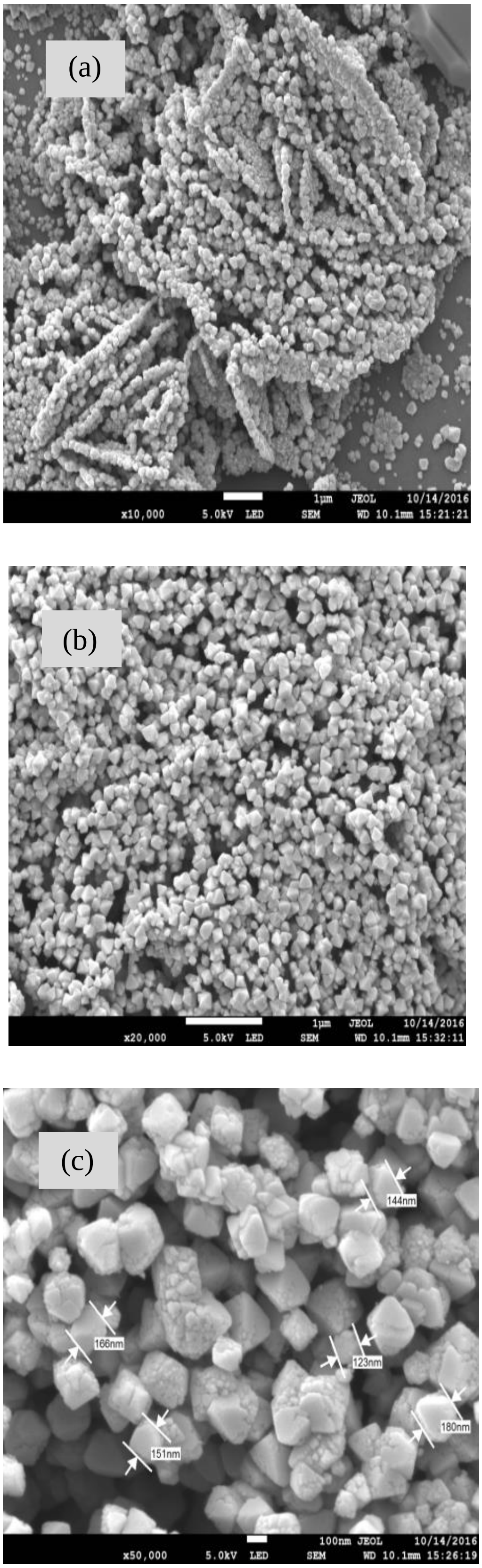


Figure 4.7. FESEM images ITO thin film at coating speed 1500 rpm at magnification of (a) 10 000 X, (b) 20 000 X and (c) 50 000 X

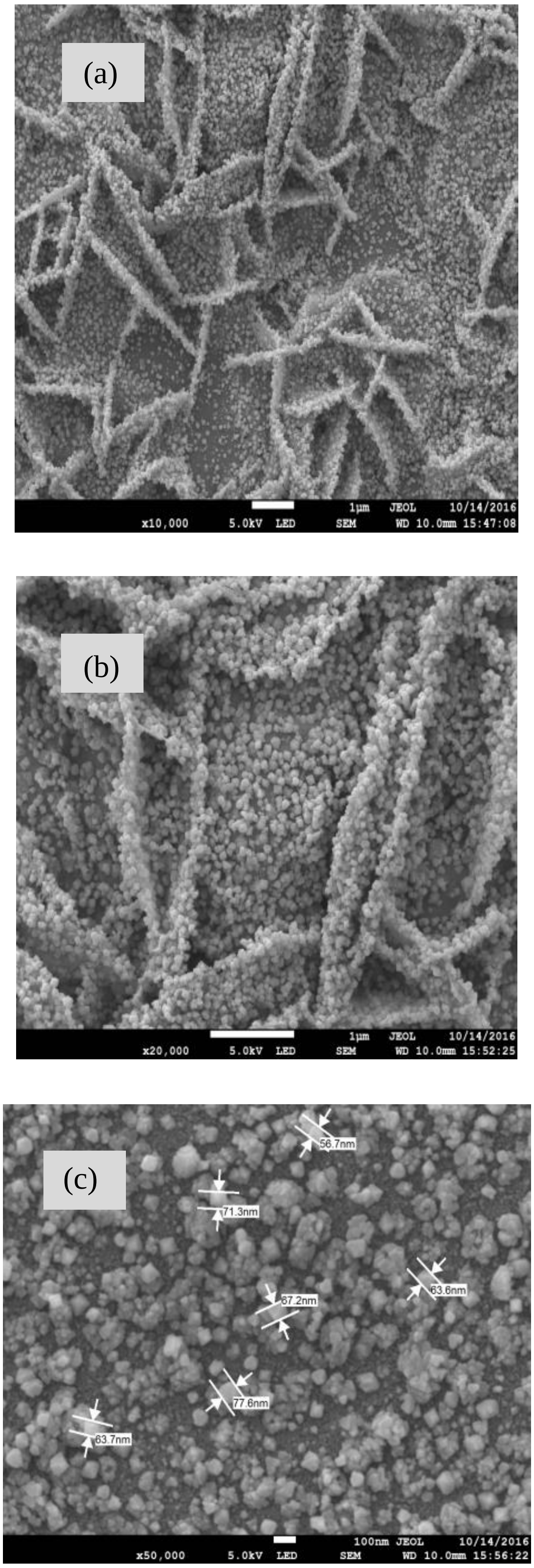


Figure 4.8. FESEM images ITO thin film at coating speed 3000 rpm at magnification of (a) 10 000 X, (b) 20 000 X and (c) 50 000 X

The grain size decreased from 980.0 nm to 67.3 nm with increasing speed of spin coating. As speed of spin coating increase, the grain size decreased. (Table 4.3)

Table 4.3

The grain size decreased with increasing spin speed.

Speed of spin coating (rpm)	**Average grain size (nm)**
500	980.0
1500	152.8
3000	67.3

4.5 UV-VIS SPECTROSCOPY ANALYSIS

From this characterization, the result of absorbance and transmittance are produced. Figure 4.9 shows the absorbance versus wavelength spectra of ITO thin film of coating speed at 500 rpm, 1500 rpm and 3000 rpm. From Figure 4.6, all samples exhibits absorption edges in the UV region, which is between 280 nm to 350 nm.

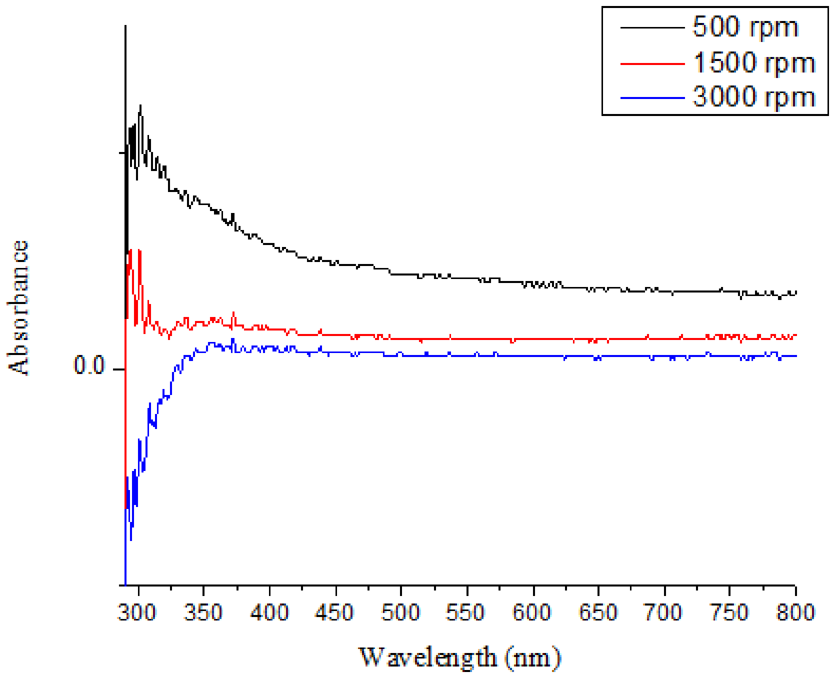


Figure 4.9. Absorbance versus wavelength spectra of ITO thin film at various coating speed

As the coating speed increases, the fundamental absorption edges of all samples are shifted towards longer wavelengths, with correspondingly lower energies (Equation 4.3)

$$e = \frac{hc}{\lambda} \tag{4.3}$$

The absorption edge of the ITO thin film at 500 rpm of coating speed occurs at approximately 300 nm, whereas for 1500 rpm and 3000 rpm at 285 nm respectively.

From Figure 4.9, the maximum absorbance of 500 rpm occurs at 310 nm, whereas 1500 rpm and 3000 rpm at 315 nm and 350 nm respectively, which means its excitonic absorption (first excitonic peak). Using OriginPro 8.6, the first excitonic peak for ITO thin films of coating speed at 500 rpm, 1500 rpm and 3000 rpm is 310 nm, 315 nm and 350 nm respectively. The wavelength indicates the wavelength of light absorbed to excite an electron from the valence band to the conduction band. Starting from approximately 380 nm and above, all samples exhibit almost completely zero absorbance, indicating the onset of high transmittance in the visible region.

Figure 4.10 shows the UV Vis spectroscopy transmittance measurement of ITO thin films with different coating speed. The transmittance value of all ITO thin films are greater than 90 % . The transmittance value in this study is slightly increased from the previous study may be due to the annealing temperature used in this study is 500 °C with deposition method is spin coating. While in the previous study, the annealing temperature used was 450 °C with deposition method is Radio Freuency (RF) sputtering. (Forat H. Alsultany*1, 2014). The increase in transmittance with increase in coating speed in the near infrared (NIR) region is due to the free carrier absorption, a phenomenon that is common in all transparent conductors having high carrier concentration (Mizuhashi, 1980).

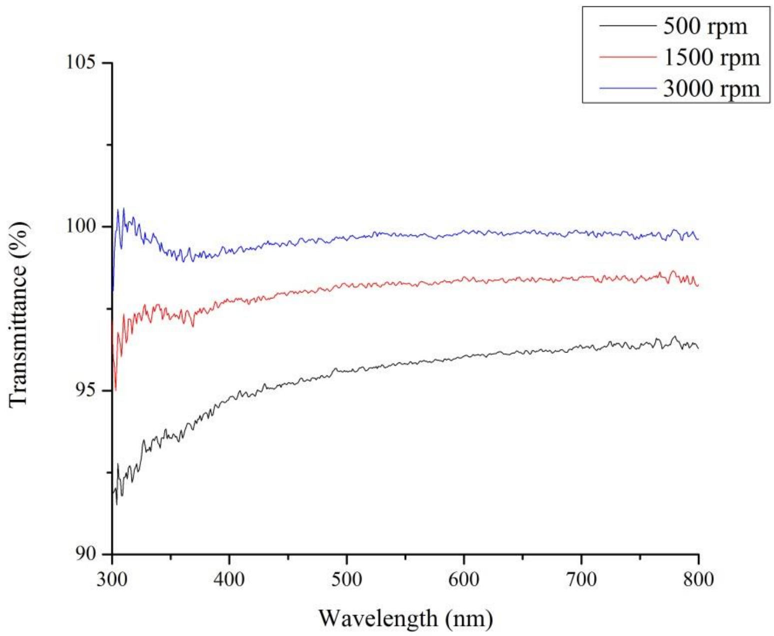


Figure 4.10. Transmittance measurement of ITO thin films at different coating speed.

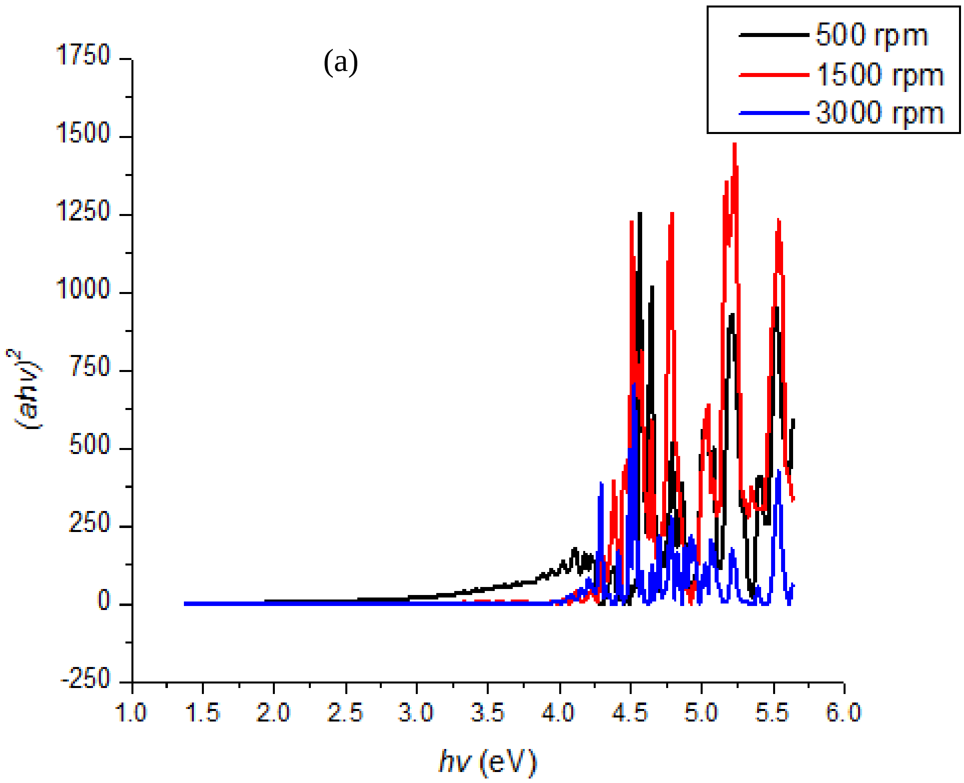
The optical band gap, values calculated from the plot of $(\alpha h v)^2$ versus hv for the ITO thin films, where α is the absorption coefficient, are shown in Equation 4.4.

$$(\alpha h v) = A\ (hv - \ E_g)^2 \tag{4.4}$$

where α is the adsorption coefficient, h is the Plank constant, A is the constant and E_g is the band gap.

Based on Figure 4.11, the Tauc plot for three samples, the band gap is range from 4.18 eV to 4.28 eV. As coating speed increases, it is observed that E_g increased from 4.18 eV to 4.28 eV.

The reported band gap from previous study is range from 3.45 eV to 3.80 eV (Forat H. Alsultany et al., 2014). It can be seen that the band gap of prepared ITO thin films slightly higher compares to the previous study. But, based on Du, et al. (2014), ITO has larger band gap around 3.5 eV to 4.3 eV. Hence, the obtained band gaps are correlated with other studies.



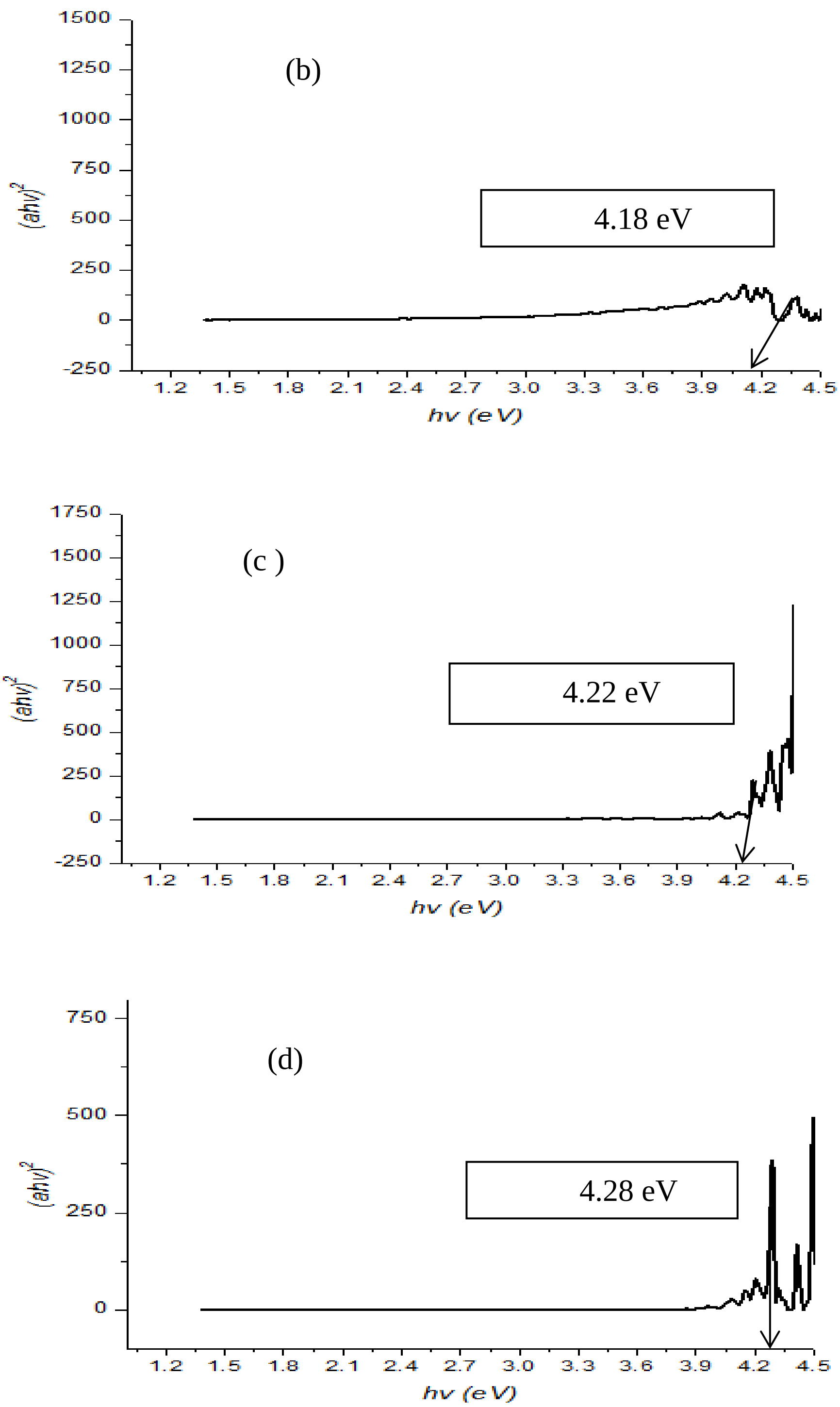


Figure 4.11. The plot of $(\alpha h\nu)^2$ versus $h\nu$ for (a) all samples, (b) 500 rpm, (c) 1500 rpm and (d) 3000 rpm of coating speed.

4.6 PL SPECTROMETRY ANALYSIS

Figure 4.12 shows the PL spectra of ITO thin films recorded under the excitation wavelength, λ = 380 nm in the 300 nm to 900 nm wavelength range. The emission peak for three samples is observed at approximately 570 nm to 590 nm. The UV emission peak is also called near band edge (NBE) emission, and it originates due to the recombination of the free exciton through an exciton–exciton collision process. A rapid decrease in the intensity of all peaks and the change of UV emission peak position confirm the substitution of Sn atom in indium sites (M. Thirumoorthi, March 2016).

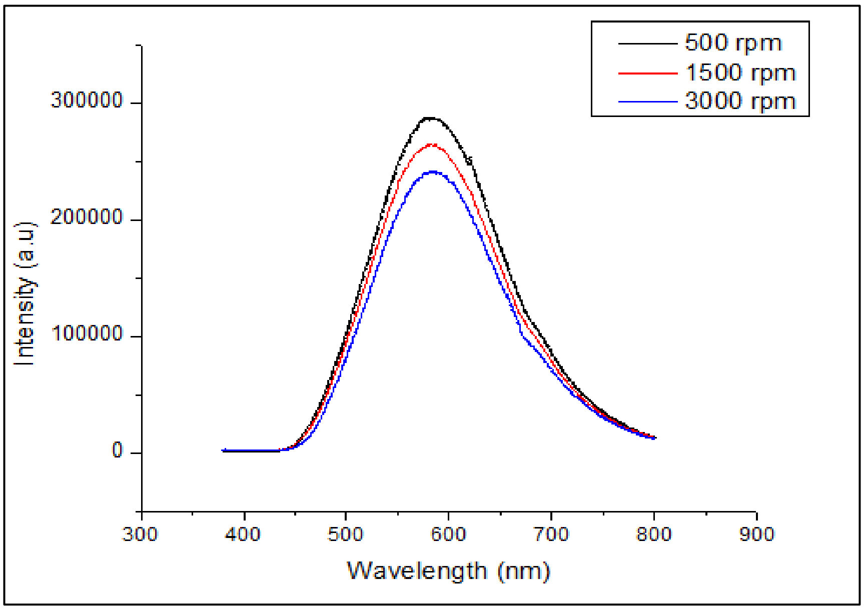


Figure 4.12. PL spectra of ITO thin films at various coating speed.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

ITO thin films with different coating speed (500 rpm, 1500 rpm and 3000 rpm) were deposited on glass substrate via sol-gel method, spin coating process at high temperature annealing (500 °C). The structural and optical properties significantly depend on the coating speed. From the XRD result obtained, the prepared ITO thin film has cubic structure, and (222) is its preferred plane. As the coating speed increase, films shows a lower degree of polycrystallinity. The calculated crystallite size of ITO thin films at coating speed from 500, 1500 and 3000 rpm is 43.54 Å, 35.92 Å and 31.98 Å respectively. The crystallite size decreases with the increase of coating speed. The grain size decreased from 980.0 nm to 67.3 nm with increasing speed of spin coating. The absorption edge of the ITO thin film at 500 rpm of coating speed occurs at approximately 300 nm, where as for 1500 rpm and 3000 rpm at 285 nm respectively. The transmittance value of all ITO thin films are more than 90%. The band gap are calculated from plotting product of adsorption coeeficients in photon energy (αhv^2) against photon energy (hv) is in the range of 4.18 eV to 4.28 eV. The PL spectra decreases, as the coating speed increased. These results showed that ITO films can be used as transparent electrode for organic light-emitting diode (OLED) and touch screen monitors, as well as in piezoelectric crystal applications.

5.2 RECOMMENDATIONS

Nowadays, ITO thin film has been widely used in many applications that provided many good properties that make them special semiconductor. There are some suggestions on how to improve its properties compared to the results obtained in this study. Firstly, choose the best parameter such as synthesis method, annealing temperature, type of substrates used and others. This parameter can be study by try and error to get the best outcomes from the results gained.

Secondly, in the stage of the preparation ITO thin film, there are some recommendations that might help future researchers to improve its properties. This include when spin coating process, the use of syringe will give unevenly distribution of deposition ITO sol-gel. Use micropipette to produce better film as it gives more accurate amount of ITO sol-gel that is needed. Next, when using furnace, set the temperature according to the desired annealing temperature to avoid the samples from damage.

Future researchers should consider all the parameter and the experimental laboratory works that might give different effect on its structural, optical and electrical properties.

REFERENCE

A Weiser, D. L. (2015). Understanding the modes of use and availability of critical metals – An expert based scenario analysis for the case of indium. journal of cleaner production 94, 376-393.

A. Pokaipisit, M. H. (2008). Influence of Annealing Temperature on the Properties of ITO Films Prepared by Electron Beam Evaporation and Ion-Assisted Deposition. Kasetsart J. (Nat. Sci.) 42, 362 - 366.

astarmathsandphysics.com. (n.d.). Retrieved from http://astarmathsandphysics.com/a-level-physics-notes/174-materials/2836-structures-of-common-solids.html

C.H. Yang, S. L. (n.d.). Thin Solid Films 516 (2008), 1984.

Du, J., Chen, X., Liu, C., Ni, J., Hou, G., Zhao, Y., et al. (2014). Highly Transparent and Conductive Indium Tin Oxide Thin Films for Solar Cells Grown by Reactive Thermal Evaporation at Low Temperature. Applied Physics A: Materials Science & Processing [Online], 117.

Fonash, W. S. (1986). Highly Conducting Transparent Undoped Indium Oxide Films Deposited Below 100~ by Activated Reactive Evaporation. Journal of Electronic Materials, Volume 15, Issue 3, pp 117-123.

Forat H. Alsultany*1, N. M. (2014). Effect of varying film thickness on the properties of indium tin oxide films after temperature annealing. International Journal of Enhanced Research in Science Technology & Engineering,Vol. 3 Issue 6, 443-446.

Ghoranneviss2, Z. G. (2015). Structural and morphological properties of ITO thin films grown. J Theor Appl Phys, 285-290.

Giusti, G. (2011). Deposition And Characterisation of functional ITO thin films.

H.S. Kwok, X. S. (1998). Pulsed laser deposited crystalline ultrathin indium tin oxide films and their conduction mechanisms. Thin Solid Films, 335(1), 199-302.

J.-C. Manifacier, M. D. (1977). Optical and electrical properties of SnO2 thin films in relation to their stoichiometric deviation and their crystalline structure. Thin Solid Films, 41(2), 127–135.

John D. Wright, N. A. (2000). Sol-Gel Materials Chemistry and Application. CRC Press.

L. Kerkache, A. L. (2010). ”Sputtered Indium Tin Oxide thin films deposited on glass substrate for photovoltaic application”. Granada (Spain).

Landolt, B. (1975). Numerical Data and Functional Relationships in Science and Technology. New Series (Springer, Verlag 11 117 bl. 64).

László K˝orösia, ∗. A. (2014). Sol–gel synthesis of nanostructured indium tin oxide with controlledmorphology and porosity. Applied Surface Science 320, 725-731.

LI Zhi-hua, K. Y.-p.-y. (2008). Effects of heat treatment on morphological, optical and electrical properties of ITO films by sol-gel technique. Transaction of nonferrous metal society of china 18, 367-371.

M Benoy, E. M. (2009). Thickness dependence of the properties of indium tin oxide (ITO) films prepared by activated reactive evaporation. Brazilian Journal of Physics 39, 629-632.

M. Thirumoorthi, J. T. (March 2016). Structure, optical and electrical properties of indium tin oxide ultra thin films prepared by jet nebulizer spray pyrolysis technique . Journal of Asian Ceramic Societies, 124-132.

M. Thirumoorthia, J. T. (2016). Structure, optical and electrical properties of indium tin oxide ultra. Journal of Asian Ceramic Societies, xxx-xxx.

M.M. El-Nahassa, E. E.-M. (2012). Thickness dependence of structural and optical properties of indium tin oxide. Materials Science and Engineering B 177, 145-150.

Melvin David Kumara, Y. C. (2015). Impact of thin metal layer on the optical and electrical properties of indium-doped-tin oxide and aluminum-doped-zinc oxide layers. Superlattices and Microstructures, Volume 82, , 499-506.

Mizuhashi. (1980). Thin Solid Films 70. 91.

R.G. Gordon, M. B. (2000). 25, 52.

Ramalingam., D. (2014, December 1). Synthesis of nanomaterials. Retrieved from Slideshare: http://www.slideshare.net/RamalingamGopal/sol-gel-synthesis-of-nanoparticles

S. Li, X. Q. (2006). Effects of temperature on indiumtin oxide particles synthesized by co-precipitation. J. Cryst. Growth 289 , 151-156.

Saliha Elmas, S. a. (2013). Optical characterization of deposited ITO thin films on glass and PET. Applied Surface Science 276, 41– 645.

Shorey, A. (2014, August 26). Glass Substrates for Advanced Packaging. Retrieved from 3DInCites: http://www.3dincites.com/2014/08/glass-substrates-advanced-packaging/

Sohrab Ahmadi Kandjani1, S. M. (2015). Inorganic–Organic Perovskite Solar Cells. Research Institute of Applied Physics and Astronomy (RIAPA), University of Tabriz, Iran.