EFFECT OF ANNEALING TEMPERATURES ON THE STRUCTURAL AND OPTICAL PROPERTIES OF INDIUM TIN OXIDE (ITO) THIN FILMS GROWN ON GLASS SUBSTRATE

SITI NORSHAZA SHAHIRA BT ROSLI

BACHELOR OF APPLIED SCIENCE (HONS)
MATERIAL TECHNOLOGY

UNIVERSITI MALAYSIA PAHANG

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SITI NORSHAZA SHAHIRA BT ROSLI

Thesis submitted in fulfillment of the requirements
for the award of the degree of
Bachelor of Applied Science (Honor) Material Technology

Faculty of Industrial Sciences & Technology
UNIVERSITI MALAYSIA PAHANG

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DEDICATION

This thesis is dedicated to my beloved family especially my dearest parents for nursing me with affections and whose always support me through ups and down since the beginning of my studies and throughout my final year project until finishing this thesis.

ACKNOWLEDGEMENTS

First of all, my thanks and appreciation to my super awesome supervisor, Madam Nabilah Alias for persevering with me as my advisor for her guidance. Thank you for your correction my mistakes and your concern by helping me solving all the problems and providing me with some ways to complete this final year project until produce a better thesis.

Big thanks to my parents, Mr Rosli Yasin and Mrs Rohana Harun for always besides me never stop encouragement to me and always givimg me motivation to be successful in whatsoever situations I have faced. Also humbly acknowledge all laboratory assistances of Faculty Industrial Sciences and Technology whose helps me a lot during laboratory works. Special thanks to Miss Atiqah for helping and providing me all necessary material and apparatus to run my lab works and also for her guidance in arranging my project's budget.

Last but not least, I must acknowledge as well my forever buddies, Amirah Athirah Sazali and Nor Sarahtul Nadirah Hairol Nizan have generously given their time to better my work. Especially, I need to express my gratitude and deep appreciation to whose friendship, and wisdom have supported, and entertained me over the many years of our friendship. I thank them for their contribution and their good-natured support to finish this project.

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ABSTRACT

Metallic oxides are one of the transparent semiconductors that having abundant application in industry. Indium tin oxide (ITO) is an example of metallic oxide which commonly referred to ITO thin films. ITO were prepared by sol-gel method which coated on the glass substrate and then annealed in the various temperatures of in the range 300 to 500 ℃ in order to improve their structural and optical properties. In this study, the characterization techniques of X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), UV-visible (UV-Vis), and photoluminescence (PL) spectra measurements were performed to investigate the effects of substrate on the structural and optical properties of ITO thin films. For structural properties, the XRD results indicated that the highest intensity peak for the highest annealed treatment, 500 ℃ ITO thin film is (222) while for the lowest annealed treatment, 300 ℃ have no peaks appeared at all. While FESEM characterization showed the grain size ITO thin films for the highest annealing temperature, 500 ℃ is bigger compared to the grain size of ITO thin films annealed at 300 ℃. For optical characteristics, UV-Vis analysis shows the band gap plotted from the Tauc's plot give that the energy band gap of each samples are from 4.1 eV to 4.5 eV. For Photoluminescence spectroscopy, it can be evidently seen that for all ITO films samples, there is an UV emission peak at approximately 535 nm and 585 nm.

ABSTRAK

Logam oksida ialah salah satu semikonduktor lutsinar yang digunakan secara meluas dalam industri. Indium timah oksida (ITO) ialah satu contoh logam oksida yang biasanya dirujuk kepada filem nipis ITO. Filem nipis ITO disediakan melalui kaedah sol-gel yang mana dilapisi di atas substrat kaca dan dibakar pada suhu berlainan dalam lingkungan 300 ℃ sehingga 500 ℃ untuk mengkaji struktur dan ciri-ciri optic mereka. Teknik-teknik pencirian seperti sinaran x-ray (XRD), imbasan mikroskop elektron (FESEM), spektroskopi ultraviolet (UV-Vis) dan spektrum fotoluminasi (PL) telah digunakan untuk mengkaji bagaimana penggunaan suhu yang berbeza memberi kesan kepada struktur dan ciri-ciri optic filem nipis ITO. Untuk ciri-ciri struktur, hasil sinaran x-ray menunjukkan keamatan tertinggi bagi filem nipis ITO pada pembakaran suhu tertinggi, 500 ℃ ialah (222) manakala bagi filem nipis ITO pada pembakaran suhu terendah, 300 ℃ tidak menunjukkan sebarang keamatan. Imbasan mikroskop elektron menunjukkan saiz zarah filem nipis ITO pada pembakaran suhu tertinggi lebih besar berbanding saiz zarah filem nipis ITO pada pembakaran suhu terendah. Untuk sifat-sifat optik, analisis UV-Vis menunjukkan jurang jalur untuk setiap sampel ialah di antara 4.1 eV ke 4.5 eV. Untuk spektroskopi fotoluminasi, terdapat pemancaran ultraungu pada 535 nm and 585 nm untuk semua sampel dengan suhu pembakaran yang berbeza.

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LIST OF SYMBOLS

^{o}C	-	degree celcius
Å	-	angstrom (10^{-10})
g	-	grams
h	-	hour
t	-	time
%	-	percent
λ	-	wavelength
2θ	-	Bragg's angle
α	-	absorption coefficient
β	-	FHWM
h	-	Planck's constant
v	-	frequency

LIST OF ABBREVIATIONS

ITO	-	indium tin oxide
CBD	-	chemical bath decomposition
CVD	-	chemical vapor deposition
FESEM	-	field emission electron scanning microscopy
PL	-	photoluminiscence
XRD	-	X-ray diffraction
UV-Vis	-	ultraviolet-visible
FHWM	-	full half width maximum
SnO	-	tin oxide
SnO_2	-	tin dioxide
Sn	-	tin
$InCl_3$	-	indium chloride
Cu-Kα	-	copper K-alpha
rpm	-	rotation per minute
Eg	-	band gap energy
g	-	grams
h	-	hour
cm	-	centimeter (10^{-2})
eV	-	electron volt
kV	-	kilovolt
mA	-	milliampere
nm	-	nanometer (10^{-9})
μL	-	micro liter

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION TO INDIUM TIN OXIDE (ITO)

Straightforward semiconductors, particularly metallic oxides, are of incredible application in industry. One of them is indium tin oxide (ITO), which other than having great conductivity, has a high straightforwardness over the visible spectrum. These qualities can be abused in ITO straightforward electrodes, films in solar cells, warmer windows and uncommonly in the production of the organic light-emitting diode (OLED) (H.Y Valencia et al., 2008).

ITO is a standout amongst the most generally utilized straightforward directing oxides due to its two primary properties, which are structural and optical straightforwardness, and the simplicity with which it can be saved as a thin film (Solieman A, Aegerter M A., 2006). ITO thin films are most normally kept on surfaces by physical vapor testimony.

ITO is thought to be optoelectronic material that is connected broadly in both exploration and industry. It can be utilized for some applications, for example, level board shows, brilliant windows, polymer-based hardware, thin film photovoltaic, and structural windows (T.F. Stoica et al., 2003) . In addition, ITO thin films for glass substrates can be useful for glass windows to ration vitality and green tapes are used for the creation of lights that are electroluminescent, practical, and completely adaptable (Harith Ibrahem, Mariam Moghdad, 2013).

They are additionally utilized basically to serve as coatings that are against intelligent and for liquid crystal display (LCD) and electroluminescence, where the thin films are utilized as leading, straightforward terminals (Jaeger, 2002).

This thin films are consistently used to make direct conductive coatings for presentations for examples, fluid gem shows, level board shows, plasma shows, touch boards, and electronic ink applications (Solieman A, Aegerter M A., 2006). Moreover, they are additionally utilized as a part of natural light-discharging diodes, sun based cells, and electromagnetic interference (EMI) protecting (Jaeger, 2002). ITO are used as the anode (opening infusion layer) in organic light-emitting diodes (OLED) (Alam M J, CAMERON D C, 2002). Historically, the best ITO films need extra fine designing when they are utilized as a part of the solid coordinated contraption in order to acquire indicated fine examples. They are hard to acquire a fine example at a sub-nanometer scale through traditional synthetic drawing techniques, for example, wet carving (Harith Ibrahem, Mariam Moghdad, 2013).

Thus, in this study the properties of ITO deposited on the glass substrates which are annealed at various temperatures (300, 400 and 500 ℃). In particular, we have focused on morphologies and optical properties of ITO thin films.

1.2 PROBLEM STATEMENT

There are numerous methods used to store the substance on different surfaces. A standout amongst the most widely recognized systems is the physical vapor testimony method. The other normal strategy utilized as a part of keeping the thin film on different surfaces are the sputter deposition technique.

At times, the materials may themselves be changed from their normal state by building their microstructrue through annealing. For this study, ITO thin films which are grown on glass substrate will be fabricated by sol-gel method with different annealing temperatures on the modification made on the structural and optical properties will be observed.

Hence, the investigation effect of annealing temperature for below 350 °C on the properties of structural and optical ITO thin film is rarely reported so, it gives an opportunity to carry out this study on the impact different annealing temperatures to the microstructure and optical properties of ITO thin films.

1.3 OBJECTIVES OF RESEARCH

The objectives of this research are:

1. To synthesize the thin films of ITO deposited on glass substrates by sol-gel method.
2. To analyze the effect of various annealing temperatures toward structural properties of ITO thin films using x-ray diffractometer (XRD) and field emission scanning electron microscopy (FESEM)
3. To determine the energy band gap of ITO thin films and study their optical effect on different annealing temperatures using UV-Vis spectroscopy and photoluminescene (PL) spectroscopy.

1.4 SCOPE OF STUDY

The highlighted points of this contribution are to analyze the influence of various annealing temperatures on the structural and optical properties of the annealed ITO thin films. The annealing of ITO will be obtain at a duration of one hour at different temperatures in the range (300-500) ℃. For structural, the characterization for the crystalline structures, surface morphologies and grain sizes of ITO films using XRD and FESEM. Apart from that, for optical studies investigation on the energy band gap, absorption of light and emission of light for ITO films using UV- Vis spectroscopy and PL spectroscopy.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

The worldwide purchaser gadgets industry is continually developing as indicated by the client needs and patterns. There is developing interest for cutting edge gadgets that give a mix of vast measured capacitive touch screens, with expanded affectability to touch and high level of adaptability to give a superior client experience. In spite of the fact that indium tin oxide (ITO) are the most generally utilized material as a part of showcases. This test drives the need to create elective materials to them that can convey better execution attributes. Furthermore, the investigation influence of annealing temperatures on the properties of microstructure and optical ITO thin films are entirely normal for this worldwide. Truth be told, there are such a variety of examination papers talking about how does heat treatment have changed the microstructure and optical properties of ITO thin films (LI Zhi-hua et al., 2007).

The sol-gel technique is one of the possibility for the fabrication method for ITO films, a resulting heat treatment at a generally high temperature is required for crystallization and evacuation of remaining natural historically, different illumination strategies utilizing enthusiastic particles and ultraviolet (UV) light were connected to change of sol-gel as a distinct option for annealing treatment. These studies uncovered that electronic excitation can be sol-gel determined films at low temperatures. Previous research demonstrated that the best result for annealing temperature is around 550 °C (Harith Ibrahem, Mariam Moghdad, 2013).

2.2 FABRICATION PROCESS

Abundance fabrication techniques have been used to get ready ITO thin films for examples, splash pyrolysis and magnetron sputtering (Salunkhe, R.R et al., 2009). However, sol-gel technique is the most generally utilized the path as a part of the union of ITO because of its straightforwardness and its capability to be utilized for extensive region deposition. Sol-gel method has additionally been accounted to offer great photocatalytic properties and just economical instrumentation (Hench, L.L et al., 1990). The creation of them utilizing the ease sol-gel spin coating method will be helpful in different applications based on its high transmittance in the noticeable reach and n-type conductivity. The nature of them are also can be further extemporized by carrying out annealing process on them. The technique adapted to fabricate the ITO thin films in this study is the sol-gel method.

2.2.1 Sol-Gel Method

In material science, the sol-gel process is a technique for delivering strong materials from small particles. The technique is used for the manufacture of the oxides of silicon, metal oxides and titanium (Hanaor, D.A.H et al, 2012). The sol-gel procedure is additionally a wet-compound method utilized for the manufacture of both shiny and ceramic materials. In this procedure, the sol (or arrangement) develops bit by bit towards the development of a gel-like system containing both a fluid stage and a solid stage. Regular antecedents are metal alkoxides and metal chlorides, which experience hydrolysis and polycondensation responses to shape a colloid. The essential structure or morphology of the solid stage can run anyplace from discrete colloidal particles to consistent chain-like polymer systems (Brinker, C.J et al., 1990).

The sol-gel technique is an elastic arrangement procedure for making quality materials, including earthenware creation and regular inorganic cross breeds. All around, the sol-gel process incorporates the move of an answer system from a liquid ‘sol’ (for the most part colloidal) into a solid ‘gel’ stage. Using the sol-gel process, it is conceivable to create propelled materials in a wide assortment of structures: ultrafine or circular molded powders, thin film coatings, strands, permeable or thick materials, and to a high degree permeable aerogel materials. An outline of different sol-gel procedures is represented beneath in a graphical structure (Hench, L.L et al., 1990).

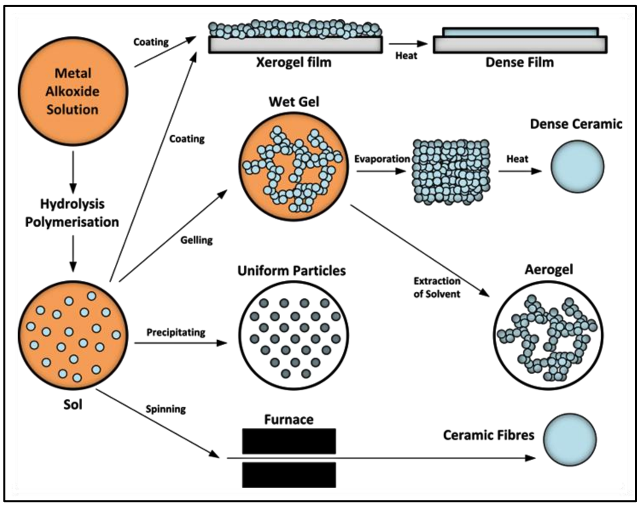


Figure 2.1. Process of Sol-gel Technology and Products
Source: Reproduced from (Claudionico, 2013)

2.2.2 Deposition Method

During the study deposition method plays a significant role in order to produce very uniform sample thin films. Thus, most of the past researcher use spin coating for doing laboratory work. Spin coating is a process used to deposit uniform thin film to level substrates. Generally a little measure of coating material is connected on the focal point of the substrate, which is either spinning at low speed or not spinning at all. In the spin coating process, the substrate spins around an axis that should be perpendicular to the coating area. The spin-on process has been developed for the so-called spin-on glasses in microelectronics and substrates with a rotational symmetry for example, optical lenses or eyeglass lenses (S.M.Attia, 2002). The stages of the spin coating process are shown schematically in Figure 2.2. The process are carried out in four stages which are deposition of the sol-gel, spin up, spin off and gelation by solvent evaporation.

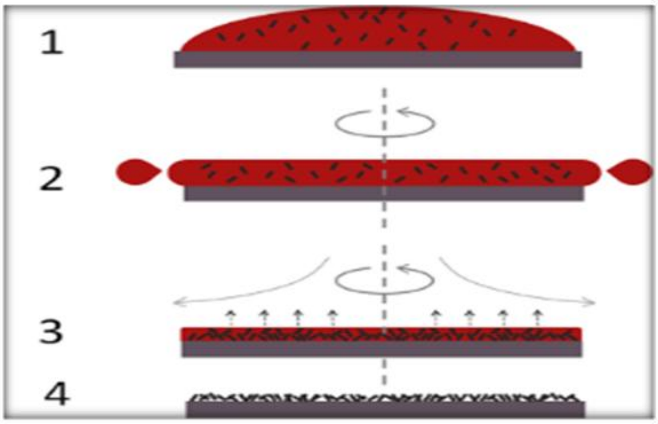


Figure 2.2. Spin coating for a little molecule in solution by a static dispense
Source: Reproduced from (M.A. Hadi Hassan et al., 2010)

2.2.3 Annealing Treatment

Annealing is defined as a heat process whereby a material is heated to a specific temperature and then allowed to cool down slowly. A part from that, stress relief annealing is the large castings or welded structures tend to possess internal stresses caused mainly during their manufacture and uneven cooling. This internal stress cause brittleness at isolated locations in the castings or structures, which can lead to sudden breakage or failure of the material. This process involves heating the casting or structure to about 650°C. The temperature is maintained constantly for a few hours and allowed to cool down slowly (Kkaarthic et al., 2009).

Then, for using glass as the substrates it must be completely cleaned before deposition. Based on Harith Ibrahem, Mariam Moghdad, 2013, stated that the cleaning of the substrates were done utilizing deionized water, then they immersed in the ethanol and put in an agitated ultrasonic bath at least for half hour, finally the substrates dried using dry air and lens paper. The delivered film from the deposition process need to be annealed to get the fully oxidization process and put samples into the furnace for one hour which are under different annealing temperatures for different samples in the range (350-500) °C and then leave it in the furnace until it reached to the room temperature.

Besides, ITO thin film with high optical straightforwardness and high crystalline quality are vital for the greater part of the applications. Subsequently, thermal annealing is comprehensively used to upgrade the crystal quality by decreasing imperfections in the thin film. Amid the annealing process of thin film, separations and other auxiliary imperfections of the film material can be most likely disposed of (Chen, Y et al., 2012).

In term of the improvement of optical properties caused by increasing heat treatment temperature is due to the enhanced formation and crystallization of the ITO films. Higher temperature heat treatment leads to a better crystallization and lower level of defects near grain boundary, thus resulting in the improvement of structural homogeneity and the decrease of light reflection (LI Zhi-hua et al., 2007).

2.3 FUNDAMENTAL PROPERTIES OF ITO

The fundamental properties of ITO especially its optical properties have to be analyzed in order to fulfill the increased need for solid state light sources. They are extremely appealing since its principal properties optical and basic can be controlled using deposition method, requesting a watchful enhancement of the principle creation parameters for reproducible properties. The crystalline structures and the its grain sizes were concentrated on by X-ray Diffractometer (XRD) and Field Emission Scanning Electron Microscopy (FESEM).

2.3.1 The Crystalline Structure of ITO Thin Films

The XRD results demonstrated that the crystallinity of $\mathrm{In_2O_3}$ thin films are enhanced with annealing temperature. Figure 2.3 demonstrates the XRD examples of ITO heated at 200 ℃, 300 ℃, 400 ℃ and 550 ℃, individually. As appeared in this figure, when the temperature is above 200 ℃, gel on the substrate starts to lose the intermolecular water and display trademark peaks of In_2O_3. With hoisting of temperature the trademark peaks of In_2O_3 changed to be good, which proposes evident growing up of the crystalline grain. For the example relating to ITO gel heat-treated at 300 ℃, normal cubic bixbyite structure of ITO shown.

The crystal size of ITO heat-treated at 550 ℃ is figured to be around 20 nm as indicated by Scherrer mathematical statement (LI Zhi-hua et al., 2007).

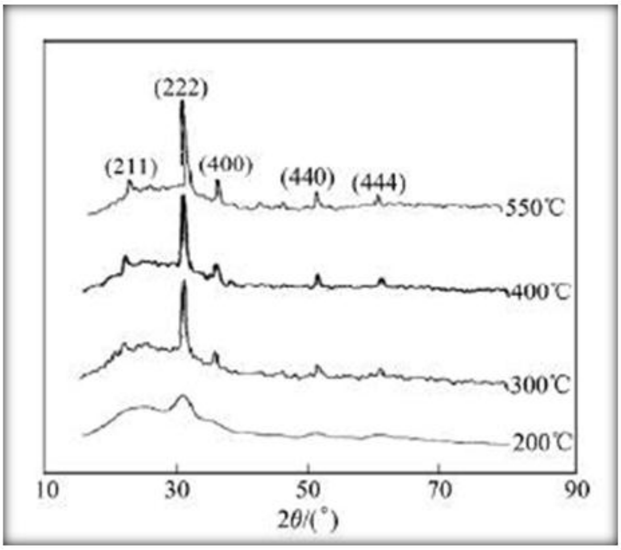


Figure 2.3. XRD patterns of ITO films heat-treated at various temperatures
Source: Reproduced from (LI Zhi-hua et al., 2007)

2.3.2 Grain Size Of ITO Thin film

The surface morphology of the electron beam evaporated ITO thin films was observed using field emission scanning electron microscope (FESEM). The expansion in grain size with the annealing treatment is because of the adequate increment in supply of warm vitality for crystallization, recrystallization and development of grains in the films. Follow the past research, stated that Nanometer-sized small grains were observed in the ITO thin films. The grain size increased as the post-thermal annealing temperature increased. The mobility of ITO thin films increased with increasing grain size. The ITO film annealed at 300 °C was an amorphous phase, while the others were polycrystalline structure (Jong Hoon Lee et al., 2015).

Based on the past research stated that the SEM surface micrographs of ITO were kept up at 600 ℃ for 1 h and cooled through various cooling techniques. As appeared in Figure 2.4, ITO films by sol-gel method have permeable structure collected by circular grains and pores consistently circulate among crystal grains. The grain size is around 20 nm and consistence with that ascertained from the XRD peak width. At the point when the ITO films are set up through air cooling, diminish in both the grain size and the porosity can be effortlessly seen, which prompts the densification of microstructure, consequently diminish in the resistivity of ITO films (LI Zhi-hua et al., 2007).

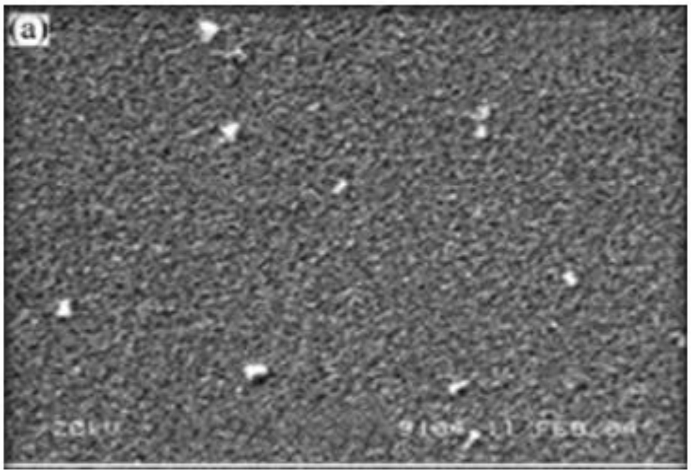


Figure 2.4. SEM surface photos of ITO films heat-treated at 600 ℃
Source: Reproduced from (LI Zhi-hua et al., 2007)

2.3.3 Optical Properties Related To ITO Thin Films

Recent studies show Indium-tin oxide (ITO) is a well-known transparent semiconducting oxide thin film. Due to its high optical transmittance in the visible and near infrared regions, and high reflectance in the infrared region, it has been widely applied in various opto-electronic devices, infrared reflectors, and display devices because of its low electrical resistivity and its wide electrochemical window, it has also been extensively used as transparent electrodes for spectroelectrochemical studies. ITO thin film is a highly degenerate n-type semiconductor (Chen, Y et al., 2012).

Optical properties of the ITO after heating at various temperatures were explored by UV-Visible spectrometer and Photoluminescence spectroscopy. High straightforwardness for the ITO in the noticeable light range is required for straightforward anode. The change of optical properties brought about by expanding heat treatment temperature is because of the upgraded arrangement and crystallization of the ITO films. Higher temperature of heating process prompts a superior crystallization and lower level of imperfections close grain limit, accordingly bringing about the change of basic homogeneity and the lessening of light reflection.

In the other hand, the energy band gap values depend on the crystal structure films, the course of action and dispersion of atoms which in the crystal lattice; additionally influenced by crystal consistency. The optical energy band gap, E_g was inferred accepting an immediate move between the edge of the valence and conduction band (Harith Ibrahem, Mariam Moghdad, 2013). A material displays high absorbance at certain wavelength locales because of its structure. That is why band gap is to be a natural property of a material, which can be changed by prerequisites, however can never be precluded or neglected.

CHAPTER 3

RESEARCH METHODOLOGY

3.1 INTRODUCTION

At this stage of the project, the purpose of this part is to explain briefly our progress conducted during lab work. This study should seek to contextualize its findings within the larger body of project. The techniques of the project must always be high quality in order to produce knowledge that is applicable outside with implications that go beyond the group that has participated in doing lab work. Furthermore, the results of our study should have implications for policy and project implementation. Thus, it is also the guidelines of the ITO thin films fabrication process which are exhibit of three main steps. Firstly, the synthesis of precursor sol to make ITO sol-gel. Secondly, the deposition of ITO films grown on glass substrate. The final step is annealing process of ITO with different temperatures on its properties of structural and optical.

3.2 FLOWCHART

Figure 3.1 summarize the flowchart of research methodology.

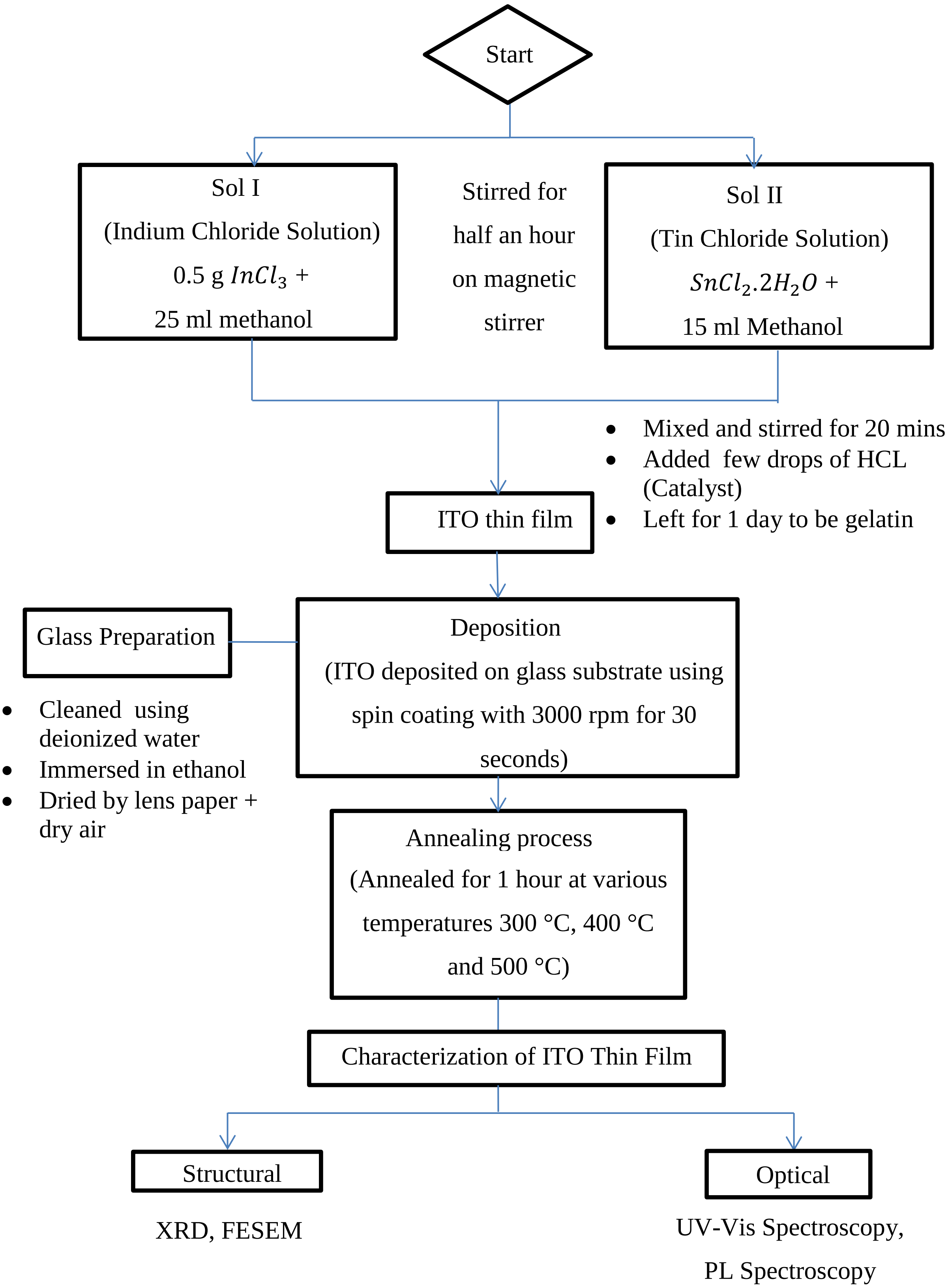


Figure 3.1. The flowchart of the guidelines for the laboratory experimental work

3.3 SOL-GEL TECHNIQUE

To prepare ITO thin film, firstly prepared Indium chloride solution (sol I) which prepared by dissolving (0.5 g of $InCl_3$ molecular weight 221.18 g/mole) in (25 ml) of methanol the solution was stirred for half hour on magnetic stirrer. The second solution was the tin chloride solution (sol II) ($SnCl_2.2H_2O$ molecular weight 225.6 g/mole) which was 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 token from the following equation $\frac{Sn}{Sn+In}$ 8%. The last solution was also stirred for half hour on magnetic stirrer, then it was added gradually to the Indium chloride solution. The final solution stirred again at least for 20 minutes a few drops of hydrochloric (HCL) acid were added as a catalyst, this solution called ITO solution. This solution needed to leave for one day to be gelation.

3.3.1 Deposition of Indium Tin Oxide Sol-Gel On Glass Substrate

Before deposition of the sol-gel, the glass substrates were washed with deionized water and immersed them in ethanol for few minutes to remove the contaminants and dried them by lens paper with dry air. After the precursor sol is left for one day aged, it was ready to use for deposition on the glass substrate. The sol-gel will be dropped on the glass substrate which must be rotated using a spin coater.

In this experiment, after doing some trial and error, a few drops of 8% $SnCl_2.2H_2O$ were deposited on a glass substrate for each coating. The spin coater is rotated at 3000 rpm for 30 seconds for each coating. The coated films were leaved for at least 1 hour before continue with annealing process to enable the films to crystallize. The procedures from coating to drying were repeated until 3 samples successive coatings are obtained.

3.3.2 Annealing Process

The prepared ITO thin film need to be annealed before proceed to characterization part. The three ITO thin films were wrapped with aluminium foil and put them into alumina bot and annealed at different temperatures (300 °C, 400 °C and 500 °C) for 1 hour each. After annealing, we need to wait for cooling process in the furnace minimum 3 hours until reached room temperature. Thereafter, the samples removed from the furnace and placed in petri dish. Thus, the films were ready for characterization process.

3.4 CHARACTERIZATION OF ITO THIN FILMS

The characterization of the as-prepared and the three samples of ITO thin films annealed at various temperatures (300-500) °C were carried out. The crystalline structure of the films were observed using two different instruments which are XRD and FESEM. While the optical properties of films were analyzed using two different instruments which are UV-Vis spectrophotometer and Photoluminescence spectrometer.

3.4.1 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) relies on the dual wave or particle nature of X-rays to obtain information about the structure of crystalline materials. A primary use of the technique was the identification and characterization of compounds based on their diffraction pattern.

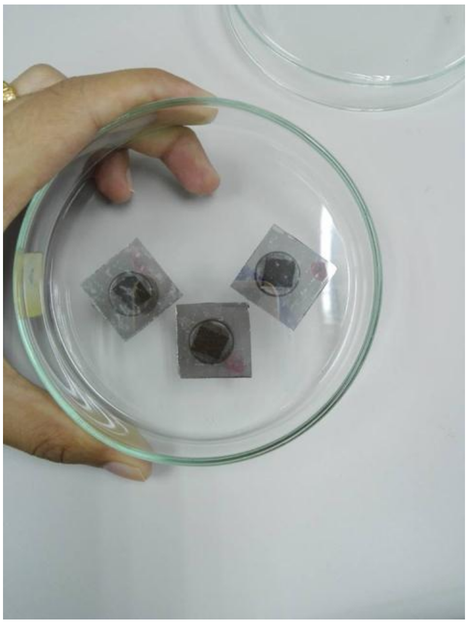
In this study, the X-ray diffractions pattern of the ITO thin films for each sample could be analyzed. Generally, the analyses evidence at low doping ratio the film has low crystallinaty comparing with other films. It will caused the intensity of the peaks decrease which means that the interaction did not reach the level of saturation which compensate between atoms (SU C et al., 2005) .

3.4.2 Field Emission Scanning Electron Microscopy (FESEM)

Field emission scanning electron microscopy (FESEM) provided topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth of field. Compared with convention scanning electron microscopy (SEM), Field Emission SEM (FESEM) produces clearer, less electrostatically distorted images with spatial resolution down to 1 1/2 nanometers – three to six times better (Graham St et al.,).

In this study, the function of FESEM were to observe the surface morphology doped ITO thin films. By comparing the images observed from FESEM for each samples, the rate of grain growth with much clearer images can be determined. However, before proceed to characterization part, the samples need to be coated with platinum first as shown in Figure 3.2 to obtain the images of crystal formed clearly.

(a)



(b)

Figure 3.2. (a) The ITO thin films coated with platinum before characterizing (b) The samples were undergoing characterizing using FESEM

3.4.3 Ultraviolet Visible Spectroscopy

The variations in the optical transmittance of the ITO thin films as a function of wavelength on the substrate temperature. The transmittance of the film was influenced significantly by the substrate temperature during the deposition process. Generally, the transmittance is closely related to a scattering effect. It is considered that an increase in substrate temperature accelerated the degree of crystallization, bringing the system to the well-developed fibrous pattern more rapidly. Accordingly, the microstructure with the fibrous pattern had a higher value of the transmittance by reducing the light scattering in the film (LI Zhi-hua et al., 2007).

In this study, UV-Vis spectroscopy was used to determine the optical properties of ITO thin films after heating treatment under different temperature and its transmittance. From the absorbance spectrum obtained, the band gap of each ITO thin film can be determined using Tauc’s plot. It is also can determine the energy band gap for each samples (Daoudi K, et al., 2003)

3.4.4 Photoluminescence Spectroscopy

Photoluminescence spectroscopy was a non-contact, nondestructive method of probing the electronic structure of materials. In essence, light was directed onto a sample, where it was absorbed and where a process called photo-excitation could occur.

In this study, photoluminescence (PL) spectrometer was used to characterize the photoluminescence property of ITO thin film by using radiation source which energy was based on the speculated absorbed wavelength.

CHAPTER 4

RESULT AND DISCUSSION

4.1 INTRODUCTION

In this part of study, the results obtained from XRD, FESEM, UV-Vis and PL Spectroscopy analyses were discussed. The discussion will be consisted of plotted graph, images, and tabulation of data.

4.2 SYNTHESIS OF ITO

Figure 4.1 shows the samples of synthesized ITO precursor solution after left aging 1 day reaction time. It supposed to get clear solution and to be gelatin form. This solution is then deposited on a glass substrate using spin coater with speed 3000 rpm for 30 seconds before proceed with annealing process. From this observation, we noticed that ITO precursor solution is already in clear solution and has a bit of odor.

Figure 4.1. Precursor of ITO solution after leaving for aging

4.3 X-RAY DIFFRACTION (XRD) ANALYSIS

The crystal structure and orientation of the ITO thin films were analyzed by X-ray Diffractometer using Cu-Kα radiation. Figure 4.2 shows the XRD spectra of the heat treatment at 300 °C, 400 °C and 500 °C for each ITO thin film respectively.

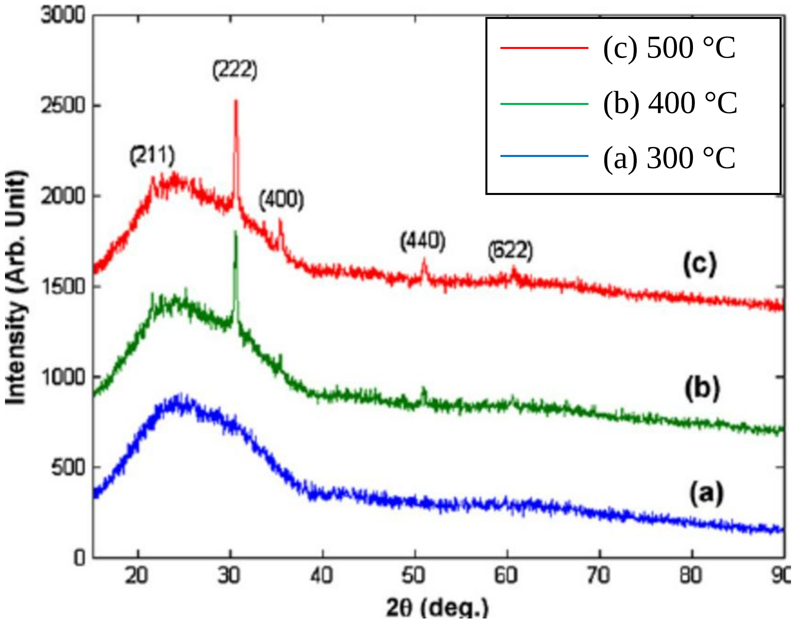


Figure 4.2. XRD spectra of ITO thin films annealed at 300 °C, 400 °C and 500 °C respectively

X-ray diffraction data showed that all films have polycrystalline nature cubic for ITO with major reflex along (222) plane. The films crystalline structure were investigated using X-ray instrument supplied by Bruker D8 Advance X-ray diffractometer using Cu-Kα radiation of 1.5406 Å in reflection geometry. A proportional counter with an operating voltage of 40 kV and a current of 40 mA is used in the (2θ) range from (20° - 90°).

Based on the XRD pattern of ITO films showed above, the analyses evidence at low heat-treated film has low crystallinity comparing with other films. Besides, we also can observed from experimental data appearing of peaks at (222), (400), (440) and (622) which refer to cubic structure of In_2O_3 the intensity of peaks are very low; this means that the interaction did not reach the level of saturation which compensate tin atoms within the structure of In_2O_3. However, no phase corresponding to tin (Sn) or other tin componds were detected showing that the Sn was in solution of In_2O_3. As a result the crystalinity increase because substitutional replacement of indium by tin in the lattice took place hence these results are consistent with other published results such as (Harith Ibrahem, Mariam Moghdad, 2013).

However, as can be seen in the Figure 4.2 (a) there is some unknown additional peaks and they might be from the glass substrate itself. The diffraction peaks observed for the lowest annealing temperature ITO film which is 300 °C are not very prominent and there is no obvious diffraction peak emerged at all. Hence, as it showed in the diagram above it just has a lot of impurities for that structure it also was indicating poor crystalline quality.

Besides, the diffraction peaks began to appear clearly for the films which were annealed at 400 °C an 500 °C as shown in diagram above. Thus, followed the past researcher stated that by increasing the temperatures of annealing treatment for the films begin to take a polycrystalline nature (Jin Soon An et al., 2004) .

From Figure 4.2 (b), the (hkl) peaks observed for ITO film annealed at 400 °C are at 2θ values of 22.0°, 30.5°, 35.0°, 51.5° which were corresponding to (211), (222), (400) and (440) planes respectively. While Figure 4.2 (c) demonstrated the XRD for the highest annealing treatment ITO films which is 500 °C obtained the diffraction peaks for this film is even more prominent and distinguished compared to the peaks observed for ITO film annealed at 400 °C. This film has five pronounced peaks at (211), (222), (400), (440) and (622) planes and its corresponding to 2θ values of 23.0°, 30.5°, 36.5°, 52.0° and 61.5° respectively.

The changes in the crystallinity are especially very profounding the ITO film annealed at 500 °C. Instead having many noticeable diffraction peaks. Hence, it is also showed enhanced intensities of diffraction peaks specifically at the (222) plane which correlated to the previous researcher proved that the peak intensities increased with increasing temperatures (Jin Soon An et al., 2004).

Then, the full width half maximum (FWHM) of the peak was wider than that of the current ITO thin film. This means that the grain of ITO sol thin film is ultrafine according to Scherrer's Equation (4.1). In this equation, the intensity peak increase significantly along with a reduction in the peak half width, indicating the growth of ITO grains. So, as the FWHM increase, the grain size of ITO films become smaller and also signifies increase crytsal quality (Sung-Jei Hong and Jeoung-In Han et al., 2003). It is indeed very evident that a good annealing treatment can hugely decrease the film strain and subsequently enhance the film strain and subsequently enhance the crystallinity of the thin films.

In addition, there is a gradual increase in grain size, *D* with increasing annealing temperature from 300 °C to 500 °C. The value of *D* is calculated using Scherrer's formula (Husna, J. et al., 2012) as shown in Equation (4.1):

$$D = \frac{0.94\,\lambda}{\beta \cos\theta} \tag{4.1}$$

Where θ is the Bragg's angle of the peak, λ (1.5406 Å) is the wavelength of the XRD and β is FWHM.

Then, the increasing D value and decreasing FWHM values is an indication of improving crystallization induced by annealing treatments.

The dislocation density, δ is also calculated using the formula provided (Nagarani and Vasu, 2013) in an Equation (4.2):

$$\delta = (\frac{1}{D})^2 \tag{4.2}$$

The amount of defects in the films can be known by calculating the δ values. As can be seen for the ITO films fabricated using sol-gel method, when the amount of dislocation density decreased, the annealing temperatures increased.

Thus, the results for the annealing temperatures, Bragg's angle, the grain size (*D*), FWHM and dislocation density (δ) of ITO thin films are shown in Table 4.1.

Table 4.1
The annealing temperatures, Bragg's angle, the grain size (D), FWHM and dislocation density (δ) of ITO thin films

Annealing Temperatures (°C)	**2θ (°)**	**FWHM (°)**	**D (nm)**	**Dislocation density ($\boldsymbol{\delta}$) $(\boldsymbol{nm})^{-2}$**
300	30.5	0.045	37.350	0.00072
400	30.5	0.023	73.075	0.00019
500	30.5	0.022	76.397	0.00017

4.4 FESEM ANALYSIS

The morphologies of ITO thin films with dopant concentration of 8 % Sn which were annealed at different temperatures (300 °C, 400 °C and 500 °C) for 1 hour each were analyzed using FESEM at magnification 20 000 xM are shown in Figure 4.3, 4.4 and 4.5, respectively. The FESEM images show that the surface morphology of ITO thin films are strongly depends on heat treatments. It is because exposing the films to annealing temperatures higher than the melting point of the substrate tends to melt and subsequently destroy the film coated on it.

Thus, the influences of annealing temperatures on the properties of structural and optical ITO films play main roles in getting quality samples. It can be clearly seen that the higher the annealing temperatures give the bigger grain size of ITO thin films. The average grain sizes for ITO thin films with different temperatures (300, 400, and 500 °C) estimated are below 500 nm.

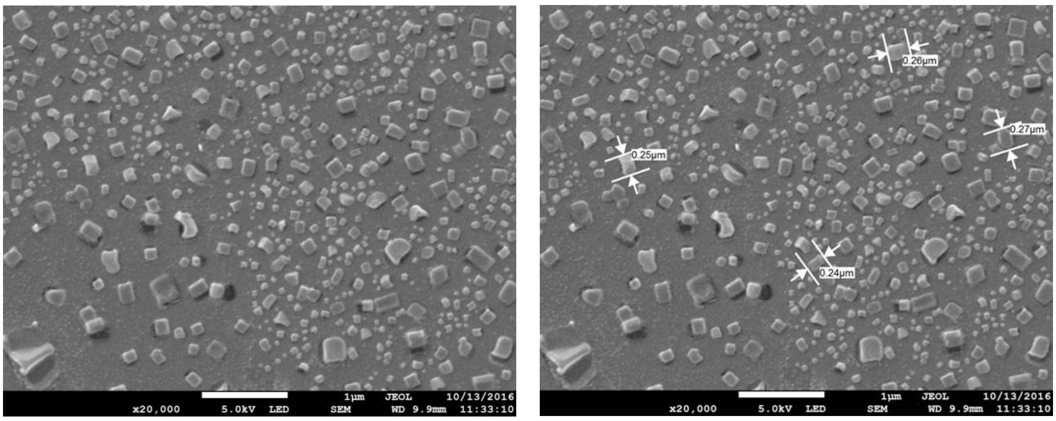


Figure 4.3. The morphologies of ITO thin film annealed at 300 °C with 20 000x Magnification

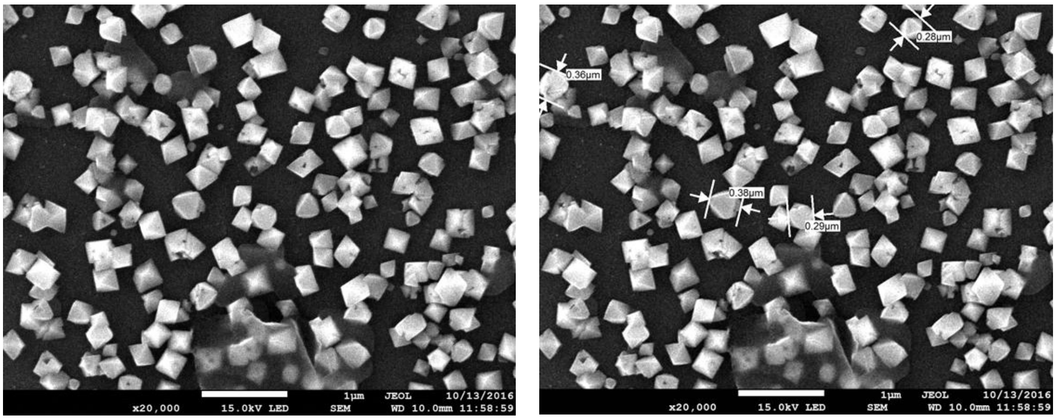


Figure 4.4. The morphology of ITO thin film with annealed at 400 °C with 20 000x Magnification

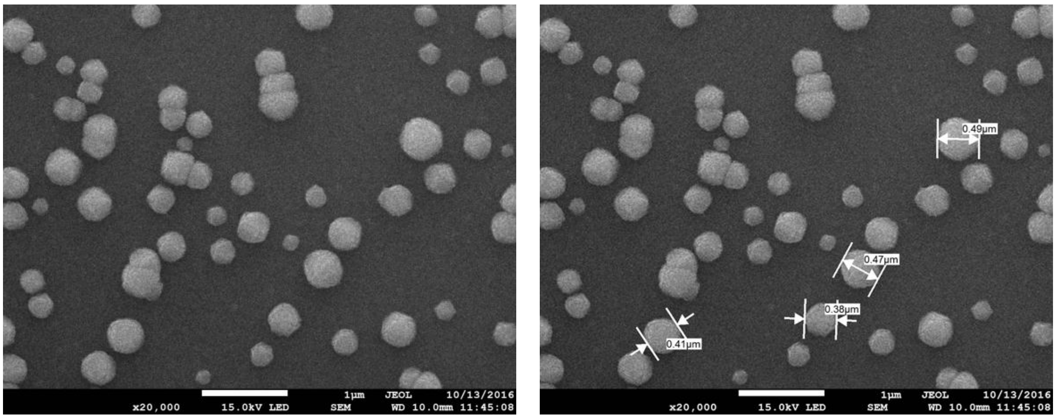


Figure 4.5. The morphology of ITO thin film annealed 500 °C with 20 000x Magnification

4.5 UV- VISIBLE ANALYSIS

There is a plotted graph of absorbance versus wavelength spectra ITO thin films annealed at different temperatures. Three characteristic spectra in the range 300 nm to 800 nm are labelled with different colours with different temperatures respectively. As can be seen from Figure 4.6, all three samples exhibits not uniform absorption edges in the UV region which is between 300 nm to 310 nm.

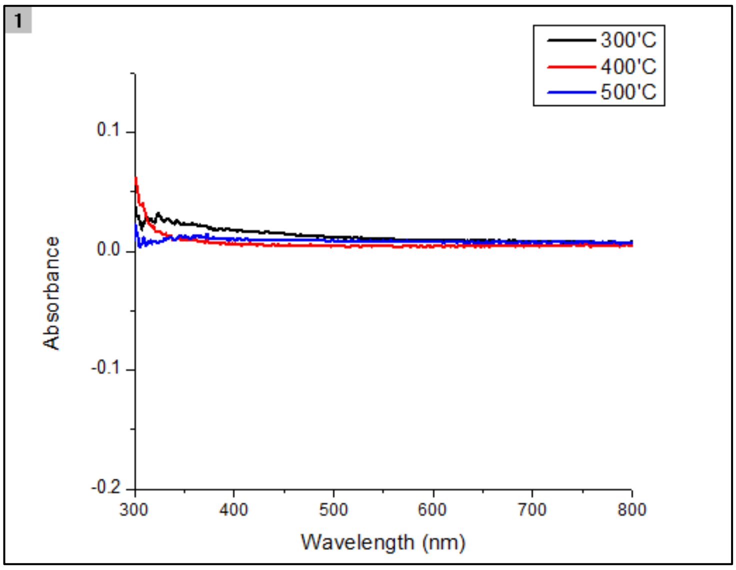


Figure 4.6. Absorbance versus wavelength spectra of ITO thin films annealed at various temperatures annealed at 300 ℃, 400 ℃, and 500 ℃ respectively

Based on the previous study, LI Zhi-hua et al., (2007) stated that as the annealing temperatures increases, the fundamental absorption edges of all samples are shifted towards longer wavelength, with corresponding lower energies, as in Equation (4.3). The extracted absorption edge plotted graph of ITO thin films annealed at 300 °C, 400 °C, and 500°C shows the approximately same value which is 300 nm. This prominent shift in the absorption edge value of all samples maybe does not correlate to the enhancement of the crytallinity and hence the quality of the film after it had been exposed to the annealing treatment may affected.

$$\mathrm{E} = \frac{hc}{\lambda} \tag{4.3}$$

Where h is a Plank costant ($4.136\ \times 10^{-15}\mathrm{eV.s}$), λ is a wavelength and c is the speed of light ($3 \times 10^{8}\mathrm{m/s}$)

The optical band gap of ITO thin films were calculated by plotting a graph product of adsorption coefficient in photon energy $(\alpha h\nu)^2$ against photon energy (hν). The band gap of ITO thin films then was determined by extrapolating graph the linear pattern of graph. In general, the optical band can also be calculated from the following equation:

$$(\alpha h\nu) = A(h\nu - \mathrm{E}_g)^2 \tag{4.4}$$

Where α is the adsorption coefficient, h is the Planck constant, A is also the constant, E_g is the band gap. The extracted band gap from plotted graph is range from 4.1 eV to 4.5 eV, which does not correlate with other studies. As can be seen in Figure 4.7, the band gap of ITO thin films for annealing temperature 300 °C is the highest while for 400 °C is slightly lower than 500 °C. However, it quite different compared to the previous study which increased in annealing temperatures will decreased in band gap. It might be caused of some errors during analyzed that samples using UV-vis and also light did not penetrate the entire precursor on the glass substrate.

The absorption coefficient, α is calculated using the Beer-Lambert law as shown in Equation (4.5):

$$\alpha = \frac{A}{t\log e} \tag{4.5}$$

Where A is absorbance and t is the glass substrate thickness (0.1 cm).

The band gap determined from the Tauc plot Figure 4.7 for the ITO thin films annealed at 300 °C, 400 °C and 500°C are 4.5 eV, 4.15 eV and 4.24 eV respectively.

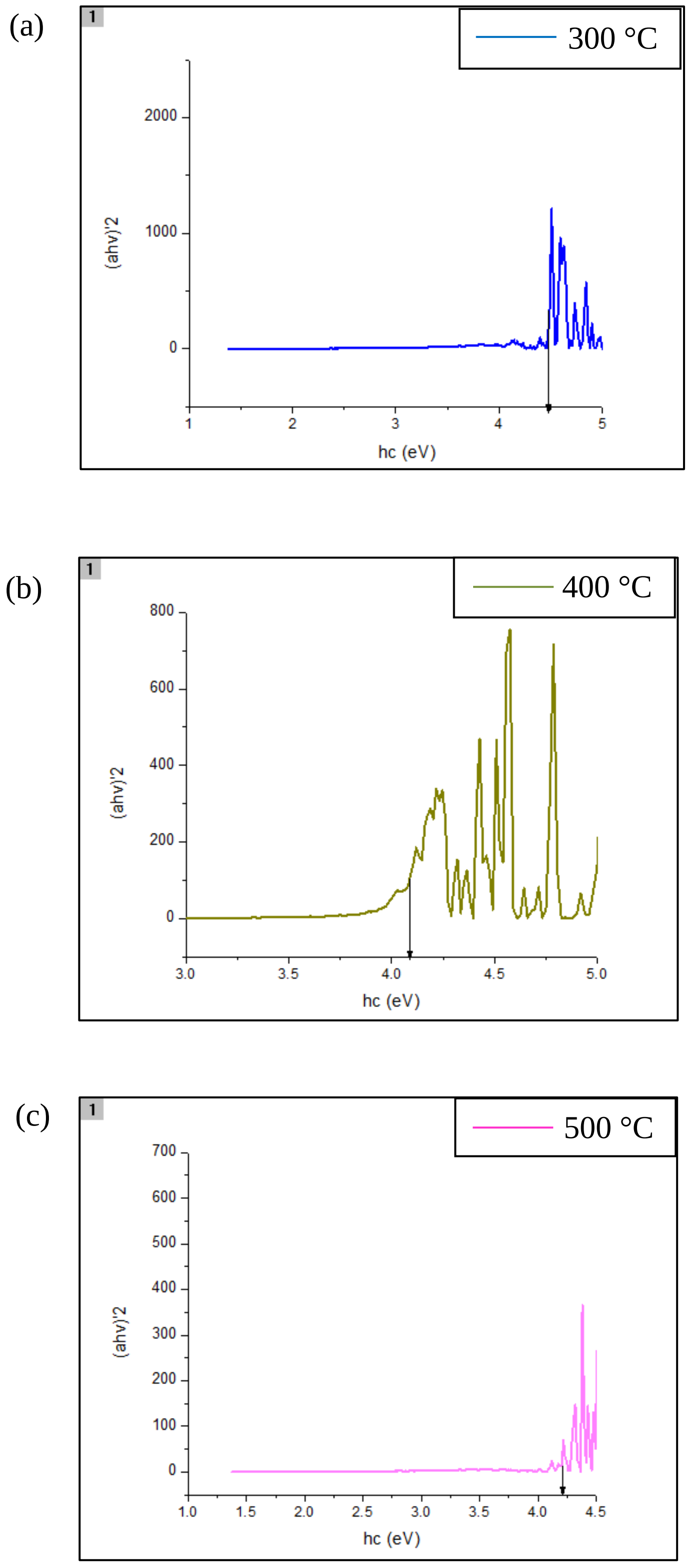


Figure 4.7. The plot of $(\alpha h\nu)^2$ against ($h\nu$) of ITO thin films annealed at 300 °C, 400 °C and 500 °C respectively

4.6 PHOTOLUMINESCENCE ANALYSIS

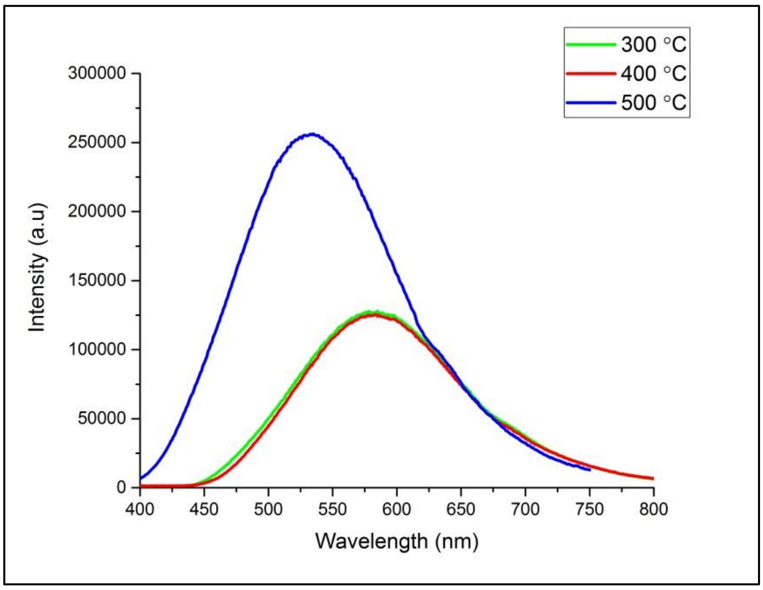


Figure 4.8. PL spectra of ITO thin films annealed at 300 °C, 400 °C and 500 °C respectively

The photon emission characteristic studied using Edinburgh Instruments FS920 PL spectroscopy (manufactured in United Kingdom); which used Czerny-Turner monochromators with high quality diffraction gratings for high dispersion and excellent imaging quality. Photolumenescence (PL) is a method which can be used to obtain data related to defects level (Lupan et al., 2010). Figure 4.8 shows the PL spectra of annealed ITO films at different temperatures in the range 300 ℃ to 500 ℃.

From Figure 4.8, it can be evidently seen that for all ITO films samples, there are observed strong ultraviolet emission peak at approximately 535 nm and 585 nm. Similar result have already been reported by H.Y Valencia et al., (2008). Therefore, it can be understood that all ITO films samples that previously absorb only UV and exhibits almost zero absorbance in the region as shown in Figure 4.6, which are able to emit UV light as well as visible light.

The emission of visible light of the highest annealing treatment, 500 °C of ITO film is extremely high compared to films annealed at 300 °C and 400 °C. Thus, the emission peak of heat-treated at 500 °C ITO film in the visible region occurred at 535 nm, indicators the emission of green light.

Besides, both ITO films annealed at 300 °C and 400 °C emitted yellow light due to its emission at a wavelength 585 nm which is a drastically lower intensity has happened compared to that ITO films annealed at 500 °C. However, the exact reason of this visible emission is still not confirmed but as Sagar,P et al., (2007) stated that oxygen vacancies are generally considered the potential defects responsible for this emission. Hence, these defects are assumed to be sensitive to annealing treatment and causing the PL emission at visible region to be sensitive to annealing treatment as well. Thus, it can be noticed that the intensity of visible emission peak is more higher than intensity of UV emission peak for all samples.

Table 4.2
Wavelength of Visible light spectrum
Source: Reproduced from (Advanced Material Laboratory)

Colour of light	**Wavelength (nm)**
Red	700 – 600
Orange	640 – 600
Yellow	600 – 570
Green	570 – 510
Blue	510 – 460
Indigo	460 – 430
Purple	420 – 430
Violet	430 – 400

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

The impact of annealing treatment on the structural and optical of ITO thin films fabricated using sol-gel method are investigated. For structural properties of ITO thin films, X-ray diffraction data showed that all films have polycrystalline nature cubic for ITO with major reflex along (222) plane. The films crystalline structure were investigated using X-ray instrument supplied by Bruker D8 Advance X-ray diffractometer. However, based on the results XRD obtained that there is some unknown additional peaks and they might be from the glass substrate itself. Moreover, the diffraction peaks observed for the lowest annealing temperature ITO film which is 300 °C are not very prominent and there is no obvious diffraction peak emerged at all.

Hence, as a conclusion that it just has a lot of impurities for that structure it is also indicating poor crystalline quality. Infact, the diffraction peaks began to appear clearly for the films which were annealed at 400 °C an 500 °C which is correlated to the past research which is increasing the temperatures of annealing treatment for the films begin to take a polycrystalline nature and able to form cubic structures. FESEM analysis shows that the grain sizes increased with the annealing temperatures increased. There are also have cubic and spherical crystalline formed.

For optical characteristics, UV-Vis analysis shows the band gap plotted from the Tauc's plot give that the energy band gap of each samples are from 4.1 eV to 4.5 eV which correlated to previous researcher stated that the band gap of ITO thin films decreased as the annealing temperatures increased Chen, Y et al., (2012). For

Photoluminescence spectroscopy, it can be evidently seen that for all ITO films samples, there is an UV emission peak at approximately 535 nm and 585 nm. Similar result have already been reported by H.Y Valencia et al., (2008). Therefore, it can be understood that all ITO films samples that previously absorb only UV and exhibits almost zero absorbance in the region, which are able to emit UV light as well as visible light.

5.2 RECOMMENDATIONS

There are some recommendation that can be study in order to improve the technique use for further researching to get clear and smooth results for characterization process. Such as the parameter use to synthesis method, concentration Sn use and time for pre-annealing treatment to have better quality ITO thin films. Besides, the annealing temperature play main role for the samples to be good in crystallinity and also important in grain growth. Moreover, each of these parameter will give different effects on the structural and optical characteristics of ITO thin films.

It has been reported that production of non-uniform and thin ITO films for heat-treated at 300 ℃ has no diffraction peak intensity at all. This is because the atoms or thinner films are lesser and inadequate for grain to coalesce into larger grains. Therefore, it us recommended that trial and error process must be carried out until the most suitable spinning speed to produce a film with desired thickness and uniformly is determined.

In addition, it is very important to determine the melting point of the substrate used before determining the most suitable annealing temperature for the ITO thin films. This is because exposing the films to annealing temperatures higher than the melting point of the substrate will cause the substrate to melt and will destroy the film coated on the substrate.

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