COMPARISON OF STRUCTURAL AND OPTICAL PROPERTIES OF ZINC OXIDE AND SILVER DOPED ZINC OXIDE THIN FILMS AT VARIOUS LAYERS USING SPIN COATING TECHNIQUE

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

SUPERVISORS' DECLARATION

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DEDICATION

I dedicate this thesis to my beloved family, supervisor, and friends for their unconditional love, unlimited support and encouragement during accomplishment of this thesis

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First and above all, I praise Allah SWT, the almighty for providing me this opportunity and granting me the capability to proceed successfully. This thesis appears in its current form due to the assistance and guidance of several people. I would therefore like to offer my sincere thanks to all of them.

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Finally, my deepest gratitude goes to my family for their unflagging love and unconditional support throughout my life and my studies. You made me live the most unique, magic and carefree childhood that has made me who I am now.

.

ABSTRACT

Pure zinc oxide (ZnO) and Ag-doped Zno (SZO) thin films were fabricated and deposited on glass substrate by sol-gel method and spin coating technique. The crystalline structure, optical transmittance and surface morphology were investigated as a function of different deposition layer. The films were subjected to annealing temperature of 300 °C. ZnO and SZO shows the dominance in the (1 0 1) direction. As the deposition number increases, the crystallinity increased meanwhile the transmittance shows a valuable results since only 10 drops of dopant could improve the optical characteristics up to 90 %. ZnO thin film shows an even distribution at 3 layers deposition when subjected to 3000 rpm spin coating and chromosome-like structure were obtained at 11 layers deposition of SZO subjected to the same parameter of spin coating technique.

ABSTRAK

Filem nipis zink oksida (ZnO) tulen dan perak-didopkan zink oksida (SZO) telah dihasilkan dan dilapiskan di atas substrat kaca melalui kaedah sol-gel dan teknik lapisan spin. Struktur kristal, pemindahan optik dan permukaan morfologi telah disiasat sebagai fungsi lapisan pemendapan yang berbeza. Filem-filem ini didedahkan kepada suhu penyepuhlindapan 300 °C. ZnO dan SZO menunjukkan penguasaan dalam arah (1 0 1). Oleh kerana bilangan pelapisan filem nipis meningkat, pembentukan kristal dilihat semakin bertambah baik manakala ujian terhadap pemindahan cahaya menunjukkan keputusan yang agak menarik kerana dengan hanya 10 titik pendopan, boleh meningkatkan ciri-ciri optik sehingga 90 %. ZnO filem nipis menunjukkan pengagihan partikel yang sama rata walaupun di 3 lapisan pemendapan apabila dikenakan 3000 salutan rpm spin dan struktur seperti kromosom diperolehi pada 11 lapisan pemendapan SZO mengikut parameter yang sama seperti sebelumnya.

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LIST OF SYMBOLS

~	-	approximately
%	-	percent
λ	-	wavelength
2θ	-	Bragg angle
^{o}C	-	degree celcius
Å	-	angstrom (10^{-10})
g	-	grams
h	-	hour
t	-	time

LIST OF ABBREVIATIONS

UV-Vis	-	ultraviolet visible spectroscopy
FESEM	-	field emission scanning electron microscope
XRD	-	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF THE RESEARCH

Indium (III) oxide (In_2O_3), indium tin oxide (ITO), tin (II) oxide (SnO), doped zinc oxide (ZnO) and indium zinc oxide (IZO) are examples of the traditional n-type materials. The application of transparent conducting oxide (TCO) is commonly made from the indium tin oxide, ITO since it is optically transparent and has ability to conduct electricity. However, ITO have some drawbacks, which is toxicity, low stability and very costly (A. Ismail et al., 2007). An alternative way to overcome the disadvantages is by selecting ZNO instead of ITO since ZNO have high potential in many optoelectronic applications and better optical, electrical and also mechanical properties (Zhang et al., 2015).

Some of the physical properties of zinc oxide are insoluble in water and appears white in colour and exist in form of powder. ZnO is one example of the inorganic compound with n-type conduction due to presence of interstitial zinc and oxygen deficiency. It is known that producing p-type ZnO is difficult because of its tendency to be n-type. ZnO is generally used in everyday life as an additive in most products and materials, such as in paints, foods, fire retardants, glass, batteries and many more.

ZnO is naturally occurs as mineral zincite, however most of ZNO are produced synthetically. Properties of ZnO that is stable in chemical structure, cheap in price, non-toxic and do not harm the environment and also having transparent behavior makes ZnO very special (Gupta et al., 2010).

Some applications involving ZnO is bipolar junction transistors, gas sensor, coatings in solar cells, photo-detectors and light emitting diode (Gómez-Pozos et al., 2016). Another special characteristic of ZnO semiconductor is having 3.37 eV band gap which is wide enough with large exciton binding energy of 60 meV (Aoun et al., 2015).

Previously, many of the researchers did an extensive study on the effect of the metal doping for zinc oxide to thin film in order to improve the physical performance. There are various dopants like Cr, Cu, Ga, Al, Ag and the other metals have been doped using a various method in the previous years. However, it is reported that Ag as a good candidate for various photocatalytic and optical applications because it has shallow acceptor level for ZnO (Kumar et al., 2016). In previous study, lithium (Li), sodium (Na) and potassium (K) were selected as candidate for p-type doping in the alkali metals (IA) group. K was selected as the best candidate (Gupta et al., 2011) amongst all of three because the radius size of Li and Na is very small and have tendency to be interstitially incorporated into ZnO. In other side, there is more attention focused for the study of doping with IB group which involving copper (Cu), silver (Ag) and gold (Au) and Ag is the most suitable candidate for p-type doping (Volnianska et al., 2009)

There are many methods of synthesizing zinc oxide thin film, for example spray pyrolysis, chemical vapor deposition, sol-gel synthesis, sputtering and atomic layer deposition. However, sol-gel method would be the most promising method because of simple preparation, low cost, easy to control the chemical composition and suitable for the laboratory scale synthesize.

Hence, in this research, ZnO doped with Ag using sol-gel method followed by spin coating technique at various layers will be synthesized. It is believed that the doping of Ag will improve the optical and structural properties of the thin films.

1.2 PROBLEM STATEMENT

There are various method can be used to prepare the zinc oxide thin films such as chemical vapor deposition, sputtering, spray pyrolysis, pulsed laser deposition and sol-gel spin coating. Based on the previous study by Bougrine et al., (2003)**,** advantages of using spray pyrolysis method are low in cost and simple technique. Moreover, they are also advanced in technology compared to other techniques. However, it is only suitable for the larger scale production of thin films meanwhile for sputtering method, the process is critical and very sensitive because the microstructure of films are influenced by the argon (Ar) gas pressure (Song et al., 2002)**.**

Another technique used in previous study is using chemical vapor deposition (CVD) (Hu and Gordon, 1991)**.** This technique produces the crystalline structure at high growth rates and suitable for surface coating for the larger scale, however there are some drawbacks of using CVD technique since this process prefer higher temperature, higher than 900 ℃ and involving complex process.

Amongst all of the method mentioned above, sol-gel method is the most beneficial and selected method in preparing the thin film due to simple deposition equipment and easy for controlling the chemical component. Other than that, the fabrication of thin films also can be done at low budget and most important thing is suitability for fabricating at small amount of laboratory scale and research purposes.

In the previous study by Xian et al., (2013), Ag-doped ZnO thin film was synthesized by sol–gel method. Then, successfully prepared ZnO precursor was doped with 2 % and 4 % of Ag. The samples were then tested for thin film application. On the other hand, in this research pure ZnO and Ag-doped ZnO will be synthesized using sol-gel method followed by spin coating technique and deposited on the glass substrate. The deposition layer varied from 3 to 11 and characterized using XRD, UV-Vis and FESEM. It is believed that the doping of Ag would improve the crystal structure of ZnO and the transmittance also would be better. Meanwhile, the doping of Ag to ZnO is assumed to yield uniform surface morphology and finer grain size.

1.3 OBJECTIVES OF RESEARCH

1. To synthesize pure (ZnO) and silver doped zinc oxide (SZO) thin films using sol gel method and spin coating technique.
2. To determine the crystalline structure of pure (ZnO) and silver doped zinc oxide (SZO) using X-ray diffraction (XRD).
3. To investigate transmission of pure (ZnO) and silver doped zinc oxide (SZO) thin films using UV-Vis spectrometry technique.
4. To study the surface morphology of pure (ZnO) and silver doped zinc oxide (SZO) thin films by Field Emission Scanning Electron Microscope (FESEM).

1.4 SCOPE OF THE RESEARCH

This study is focusing on how to synthesize pure zinc oxide and silver doped zinc oxide thin films using sol-gel method followed by the spin coating technique. The prepared ZnO and SZO sol were aged for 30 minutes. The films were deposited on the glass substrate at 3, 5, 7, 9 and 11 layers. Thin spin coating was set at 3000 rpm for 60 seconds and treated under heat at 60 °C to evaporate organic residual and solvent.

The samples were characterized using XRD to determine the crystalline structure of ZnO and SZO. In addition, the optical transmission is carried out to determine the transparency of the thin films. The optical characteristic can be studied via UV-Visible spectrophotometer. Finally, the surface and morphology of the ZnO and SZO thin films will be observed using FESEM analysis.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

This chapter gives a brief review on synthesis of zinc oxide (ZnO) and silver doped zinc oxide (SZO), the idea about the spin coating technique used and also how to evaluate the ZnO and SZO using XRD, UV-Vis and FESEM analysis. This part further evaluates the recent research advancement achieved on how the different layers of film deposition will affect on the structural and optical properties of the ZnO and SZO thin films.

2.2 SYNTHESIS OF ZINC OXIDE (ZnO)

There are various method can be used to synthesis ZnO such as physical vapour deposition (PVD), chemical vapour deposition (CVD), sol-gel process and spray pyrolysis. A study on synthesis of nano and bulk crystal of ZnO by Atul Gupta et al., (2006) is done through refluxed under distillation using an absolute ethanol. The characterization by XRD indicate the wurtzite crystalline nature of the ZnO while SEM and TEM images of the zinc oxide obtained indicate the size of the various crystals, range from about 7.8 nm to 3 mm. The result for synthesis of bulk crystal is shown in Figure 2.1.

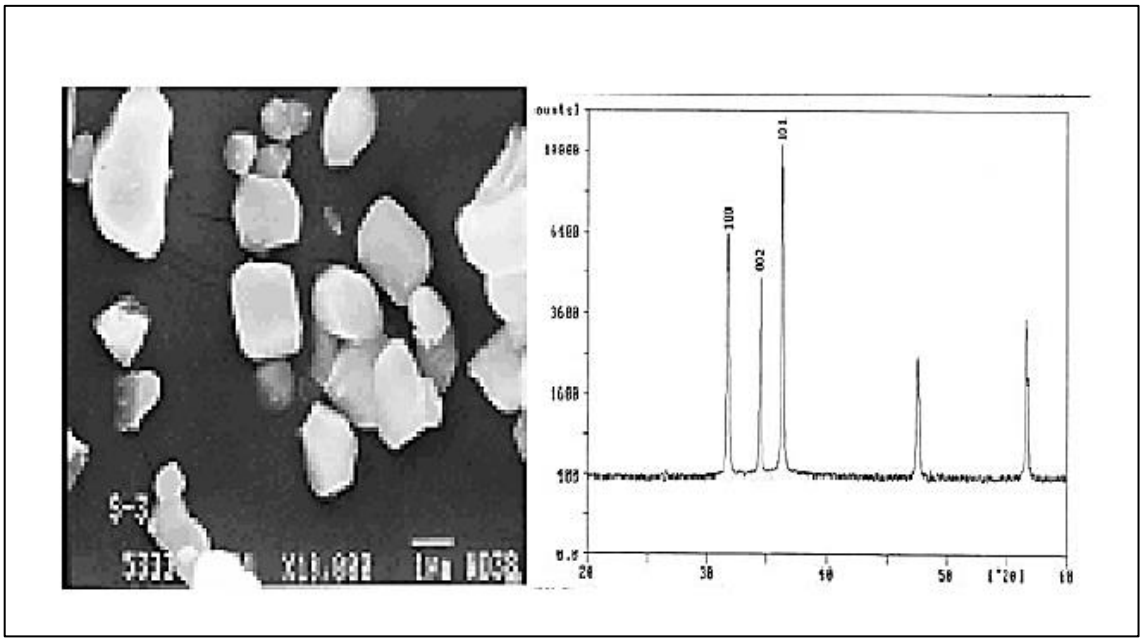

Figure 2.1. SEM and XRD of ZnO bulk crystal

Source: Reproduced from (Atul Gupta et al., 2006)

An interesting study by Sutradhar et al., (2016), showed that there are no usage of any additional capping agent or stabilizer on microwave synthesis of zinc oxide nano particles using coffee powder extract. Preparation nanocomposite of zinc oxide (ZnO) and natural graphite (NG) is done by sonication of 1:1 ratio of ZnO and NG in polystyrene solution. The resultant slurry is spread on the glass surface with aid of another glass slide. Under constant illumination, the photocurrent density-voltage measurements (I-V curves) were done by applying a potential scan from 0 V (short-circuit conditions) to the open-circuit potential for testing the solar cell performance as shown in Figure 2.2. The photovoltaic performance seems to be increase with overall efficiency (η) of 3.12 %. This improvement is due to presence of the Epigallocatechin gallate (EGCG) in the coffee extract which plays important role as both reducing and capping agent. EGCG is a very water-soluble compound and have strong polarity which gave enough reducibility to convert Zn^{2+} ions into Zn^{0} nanoparticles.

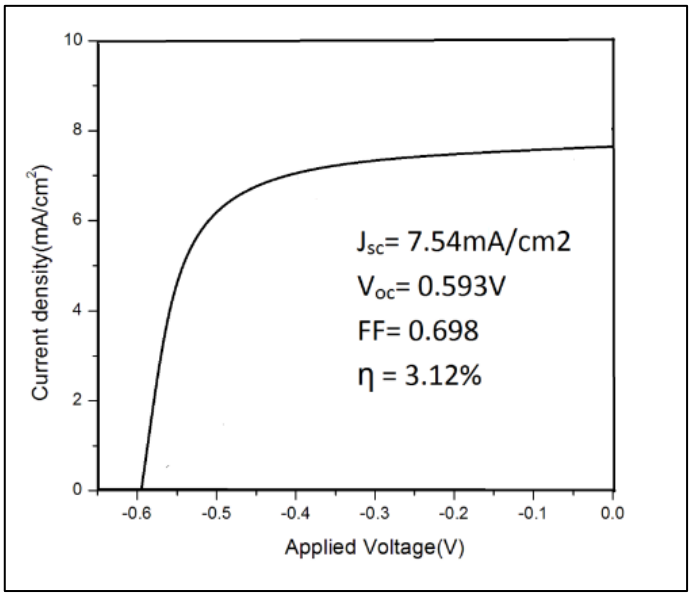

Figure 2.2. Current density versus voltage curve of thin film of ZnO/NG nanocomposite

Source: Reproduced from (Sutradhar et al., 2016)

Meanwhile, the study by Enigochitra et al., (2016) stated that substrate temperature could influence quality of the crystal, defects, band gap, orientation and morphology of the films. In this paper, ZnO thin films are prepared on various temperatures of substrate by spray pyrolysis technique with temperature of 573 K, 623 K, 673 K and 723 K, respectively. The results of deposition at temperature of 723 K shows good crystallinity compared to the lower temperature. Crystallite size also increases with increasing temperature of substrate. According to A Goswami., (1996) this kind of result attributed due to the increasing mobility of surface ad-atoms and forms cluster favourably at higher substrate temperatures. SEM micrograph shows that all thin films exhibit almost homogeneous surface morphology and smooth and rice-like grain structure. The transparency of the films decreases with increasing thickness. This result implies that at higher thickness more photons absorbed by the material.

2.3 SYNTHESIS OF SILVER DOPED ZINC OXIDE (SZO)

From previous study by Jeong et al., (2005) the silver doped zinc oxide was prepared by RF magnetron sputtering on glass substrates. In this study, different weight percent of silver (Ag) is used with silver nitrate was used as doping source. The sputtering system was pumped down to 3×10^{6} Torr using turbo molecular pump. The working pressure was 32 mTorr which was mainly in the high-purity Ar (99.99%) gas environment. The optical band gap was obtained by extrapolating the straight line in α^2 vs. hv graph where α is absorption coefficient while hv is photon energy. Since the Ag content increases, absorption edge shifted slightly to a longer wavelength and thus band gap decreases and get narrower as shown in Figure 2.3.

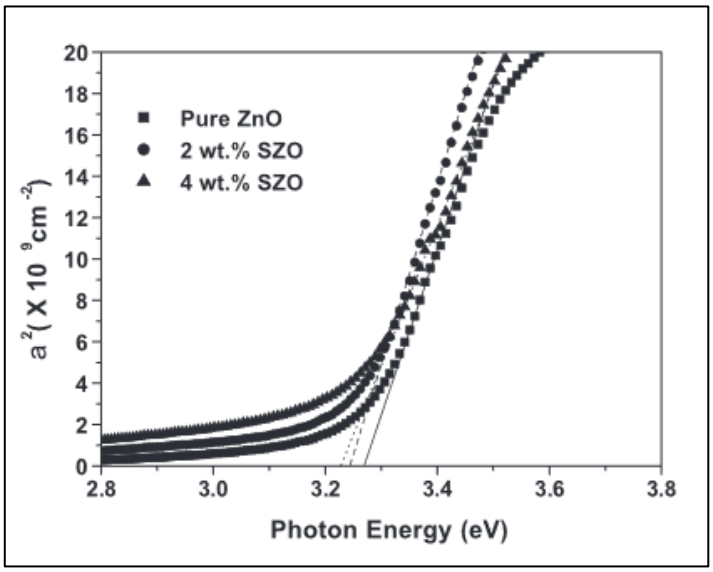

Figure 2.3. The optical band gap of ZnO and SZO at different weight percent.

Source: Reproduced from (Jeong et al., 2005)

However, the study conducted by Touam et al., (2015) on preparation of SZO thin films by sol-gel method showed totally opposite argument where in his study, the increasing amount of Ag doping in ZnO results in increasing band gap energy. Lin et al., (2005) stated that the decrement in size of the particle gives rise to the blue shift in the transition energy. It is showed that the increment in the band gap by silver doping may be attributed, on the one hand, closely related to the quantum size effect.

2.4 SOL-GEL METHOD

Sol-gel method is one examples of wet chemical process. Sol-gel method is a common method that has been used widely for sample preparation and offers lot of advantages. One of the advantages of sol-gel method is we may control the particle size. The sol particle size was controlled by manipulating the aging process of the prepared precursor and by addition of complex-forming solvent. Bitzer et al., (2016) have studied on garnet-type $Li_7La_3Zr_2O_{12}$ (LLZ) for electrolyte film for Li-ion batteries. The best results obtained when methoxyethanol (stabilizer) was added into the precursor after 30 minutes of aging time. The film was prepared using dip coating and spin coating technique.

Another study also using the sol-gel method, focused on the effect of different concentration of nickel (Ni) doping in zinc oxide thin film. The precursor solution was coated on the glass substrate by dip coating method. Ni concentration varied from 0 to 33 mol %. For XRD result analysis, peak intensity of ZnO becomes decreases, weaker and broader with increasing doping concentration (Rattana et al., 2016). It is believed that the peaks might be attributed to the $Ni(OH)^2$ phase due to Ni solubility exceeding of the limit in ZnO and the nickel formed as the secondary phase. This secondary phase also effect to the transmission spectra of the thin films, where the higher concentration of Ni leads to the decrease in transmittance and tend to make the film denser.

2.5 SPIN COATING TECHNIQUE

Spin coating is one of the most common techniques for applying thin films to substrates (Figure 2.4). The process involves depositing a few drops of precursor onto the surface of the substrate and rotated at very high speed. Spin coating is able to quickly and easily produce very uniform films from a few nanometres to a few microns in thickness. Factors that influence film thickness and other properties are drying rate, viscosity, surface tension and others. The others parameters can be taken into account are rotational speed and acceleration.

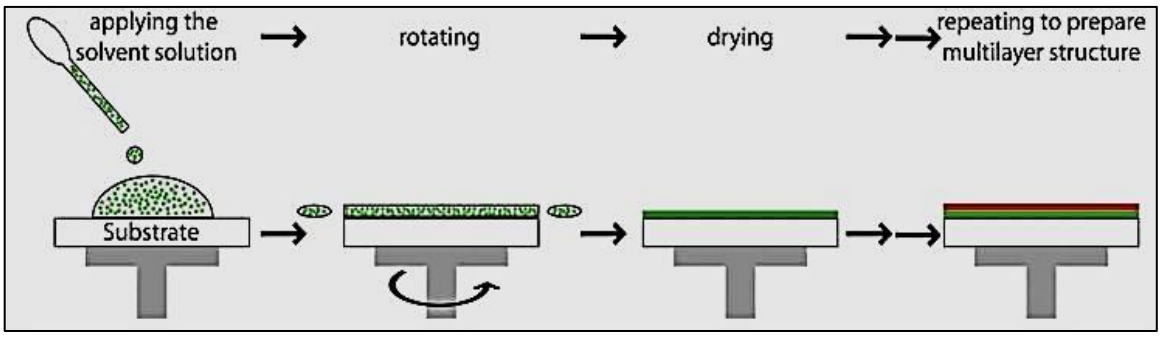

Figure 2.4. Schematic of the spin-coating process

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

One of the ways to obtain the different thickness of thin film is by applying different speed of spin coater during deposition process. Ajadi et al., (2016) has been investigated the effect of spin coating speed on the optical properties of the ZnO thin films. Different spin coating speed was used, varying from 1000 rpm to 6000 rpm for 30 second and yield the thickness from 127.4 nm and 81.5 nm. The film rotated at 2000 rpm and 3000 rpm seems to had optimum transmittance with average of 80 % and have very close value of band gap to bulk ZnO (3.37 eV).

Another study has been done on the factor of annealing temperature and spin speed effect on TiO_2 nanostructured topology and electrical properties by Affendi et al., (2015). Spin coating technique is used in this study with rate of 1000 rpm to 3000 rpm while annealing temperature is 400 °C to 500 °C.

When all of the sample subjected to current-voltage (IV-measurement) using the two-point probe method at room temperature, the highest measurement is at 425 °C annealing temperature and spin speed at 1000 rpm. This result attributed to the low roughness and small grain size of films. This situation makes the electron transportation easier since smaller grain size can fit in and usually it can be the interconnected for other bigger grains. This resolves why this film has the highest IV (Affendi et al., 2015)

2.6 ZINC OXIDE AND SILVER DOPPED ZINC OXIDE THIN FILMS CHARACTERIZATION

This section discussed about the characterization method used by the researcher using XRD, UV-Vis and FESEM analysis.

2.6.1 X-Ray Diffraction Analysis

Based on study by Cui et al., (2013) it was found that different thickness of ZnO thin film prepared by dip-coating sol–gel technique and the annealing temperature could influence the crystallinity of the ZnO thin film. In this study, five different thicknesses of thin films were obtained which were 50 nm, 150 nm, 250 nm and 350 nm. Results on XRD (Figure 2.5) shows as the thickness of film increased, the preferred (0 0 2) orientation also becomes more obvious and reach maximum at the thickness of 250 nm. However, at 350 nm the orientation becomes randomly oriented. The thinner thin films is said to have incomplete crystal growth as a few atomic layers of disordered atoms constitute to the bulk of the films. The thicker thin films, at 250 nm would contributed to the better crystallinity with preferred (2 0 0) orientation according to the crystal growth mechanism (Li et al., 2005).

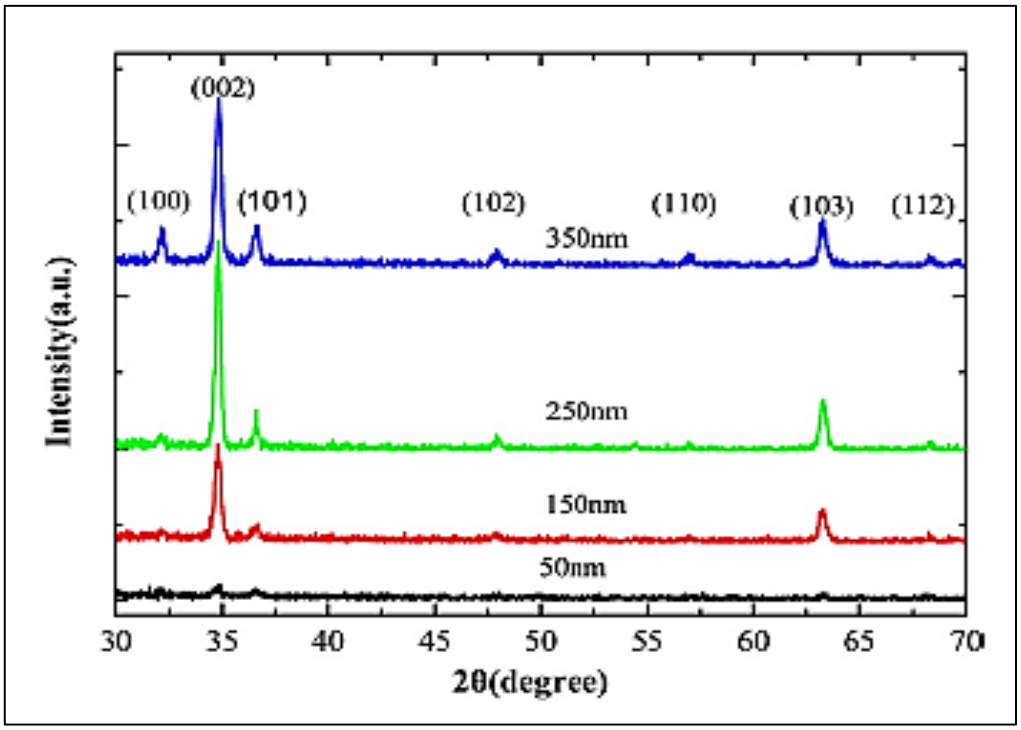

Figure 2.5. XRD patterns of the sol–gel ZnO thin films with different thicknesses annealed at 800 °C

Source: Reproduced from (Cui et al., 2013)

2.6.2 UV-Visible Analysis

Optical properties of silver doped zinc oxide thin film was studied by Dehimi et al., (2015) using low concentration of silver, which is (Ag < 1 at.%) on ZnO thin film. In this study, the precursor was prepared by sol-gel dip-coating process. Four different atomic percentage of silver was fixed at 0.3, 0.5, 0.7, and 0.9 atomic %. There is a slight decrease in transmittance for 5 at% of Ag (Figure2.6). However, for doped films with increasing concentration, they revealed better transparency with maximum average transmittance value about 86% obtained at 0.9 at.% of Ag. Therefore, using Ag doped ZnO may improve the optical quality and waveguiding properties of the films, which are directly dependent on the roughness.

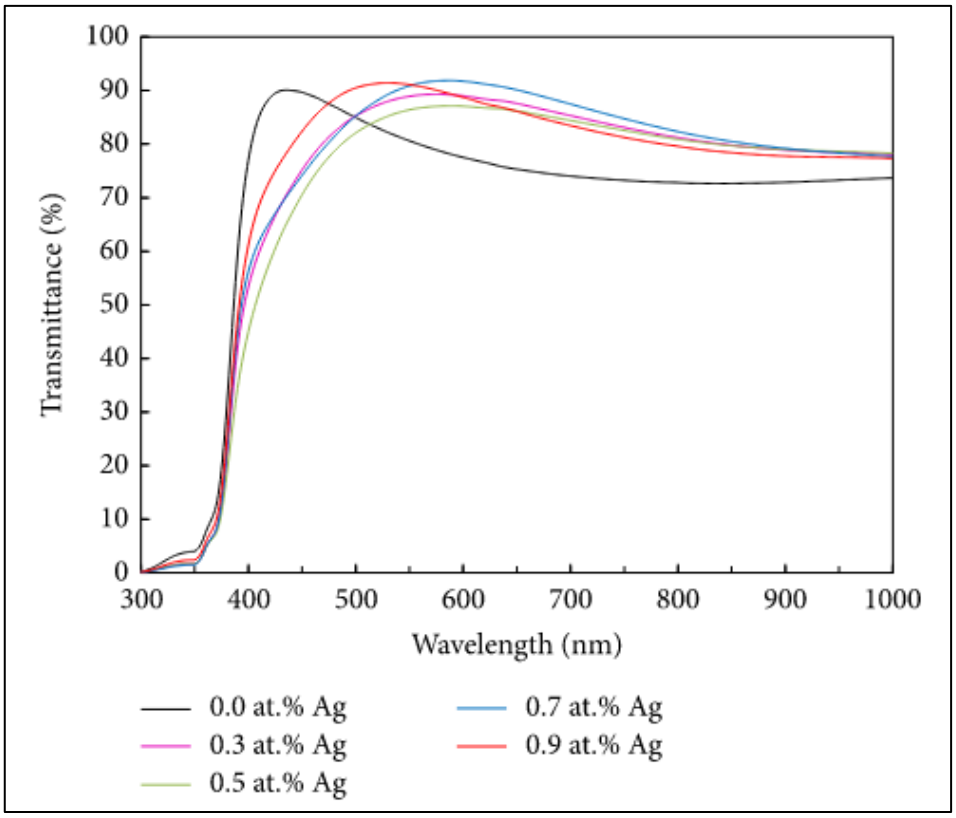

Figure 2.6. UV-Vis transmittance spectra of ZnO and SZO thin films

Source: Reproduced from (Dehimi et al., 2015)

2.6.3 FESEM Analysis

Hosseini et al., (2015) had studied the surface morphology of the pure and silver doped zinc oxide nanoparticle through FESEM analysis (Figure 2.7). The particle for pure ZnO show uniform distribution while SZO particle with 2 % and 7 % doping of Ag forms agglomeration of particles. The particle sizes were in nanoscale while the shape of particles was quasi-spherical.

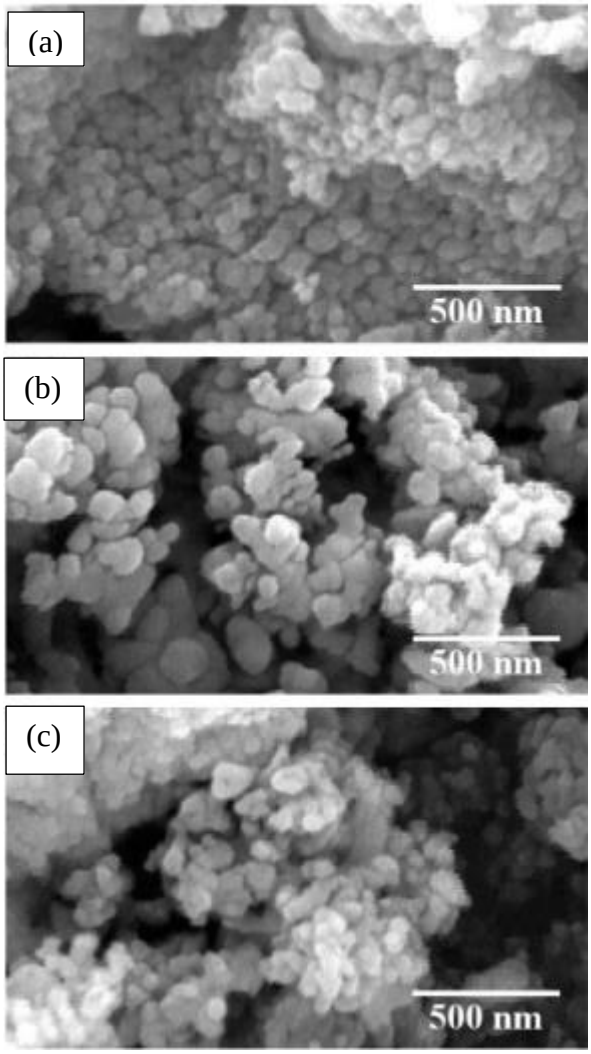

Figure 2.7. The FE-SEM morphologies of (a) pure ZnO, (b) 2 % and (c) 7 % Ag doped ZnO nanoparticles.

Source: Reproduced from (Hosseini et al., 2015)

CHAPTER 3

MATERIALS AND METHODS

3.1 INTRODUCTION

This chapter explain about the sample preparation of ZnO and SZO using sol-gel method. The preparation involve the following chemicals which are 0.015 mol of zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), 70 ml of isopropyl alcohol (C_3H_7OH), 1 ml of diethanolamine (DEA) $HN(CH_2CH_2OH)_2$, 0.169 g of silver nitrate ($AgNO_3$) and 10 ml of deionized water. Whereas, 10 pieces of 2 cm × 2 cm soda lime glass was used as substrate. Then, ZnO and SZO were coated on the substrate using spin coating technique. Lastly, the samples were characterized by observing its crystallinity, transmittance and surface morphology using XRD, UV-Vis and FESEM analysis respectively.

3.2 RESEARCH METHODOLOGY

3.2.1 Preparation of the substrates

Firstly, the soda lime glass was cut into 2 cm × 2 cm size using a diamond cutter. Decon 90, ethanol and distilled water were used as cleaning agents. The glass substrates were placed in the beaker containing mixture of Decon 90 and distilled water. Immerse it for 5 minutes. After that, they were rinsed with distilled water. The glass substrates were then immersed in the ethanol. The substrates were kept rest for 5 minutes. Finally, the substrates were cleaned with ultrasonic bath for 30 minutes. The glass substrates were dried in the drying cabinet at temperature of 80°C.

3.2.2 Pure and Silver Doped Zinc Oxide Thin Film Synthesis

There are three main processes in the thin films synthesis. The main processes are preparation of precursor solution, deposition of prepared sols on the substrates and annealing the thin films. All the process were summarised in the Figure 3.1

Flow Chart

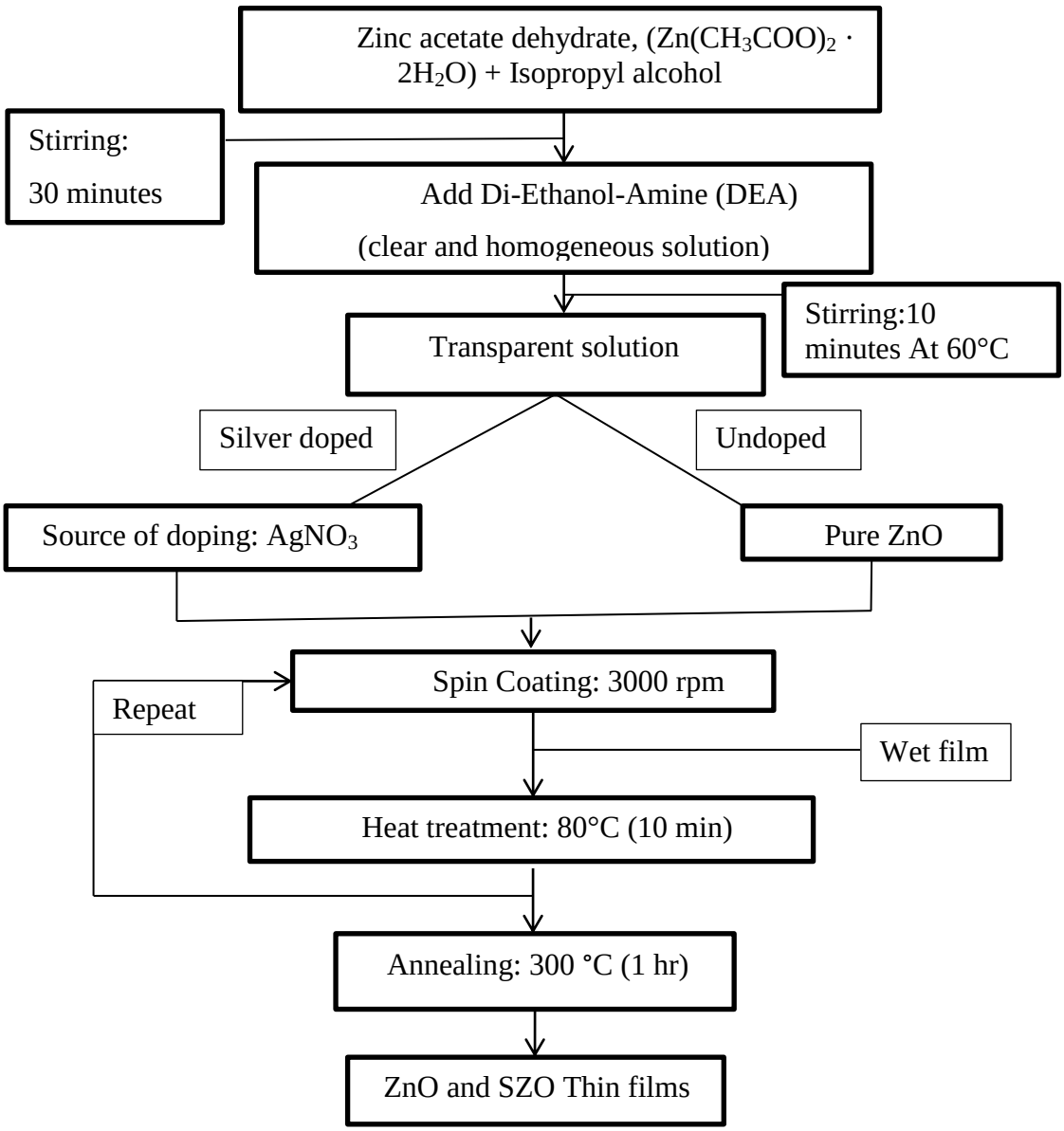

Figure 3.1. Flow chart showing the procedure for preparing ZNO and SZO thin films

3.2.3 Preparation of Precursor Solution

Zinc acetate dehydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$), isopropyl alcohol and diethanolamine (DEA) were used as starting material, solvent and stabilizer respectively. The 3.3 g of zinc acetate dehydrate was dissolved in 70 ml isopropyl alcohol. Before dissolving the solute in the solvent, zinc acetate dehydrate powder was grinded using mortar and pastel in order to obtain fine powder of zinc acetate dehydrate. The mixture was stirred thoroughly on magnetic stirrer at room temperature for 30 minutes until milky solution was produced (Figure 3.2 (a)). Under continuous stirring, 1 ml of DEA was added drop by drop into the mixture at 60 °C. DEA act as stabilizer which causes the mixture turns clear and homogeneous (Figure 3.2 (b)).

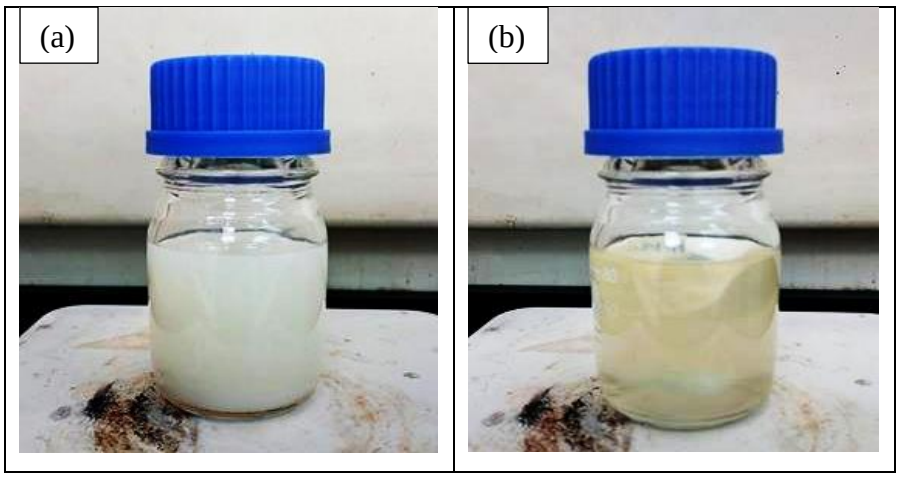

Figure 3.2. (a) ZnO solution without DEA while (b) ZnO solution with DEA

For doping source, 0.169 g of silver nitrate ($AgNO_3$) was dissolve in deionized water for 15 minutes and keep maintained at 0.1 M. Then, 10 drops of silver solution was added to zinc oxide solution and stirred for another 30 minutes. The precursor was kept in a schott bottle. To prevent any reactions occur, the schott bottles were wrapped with aluminium foil and aged for 30 minutes at room temperature. The pure and silver doped solutions were ready to be deposited on the glass substrate as shown in Figure 3.3 (a) and (b).

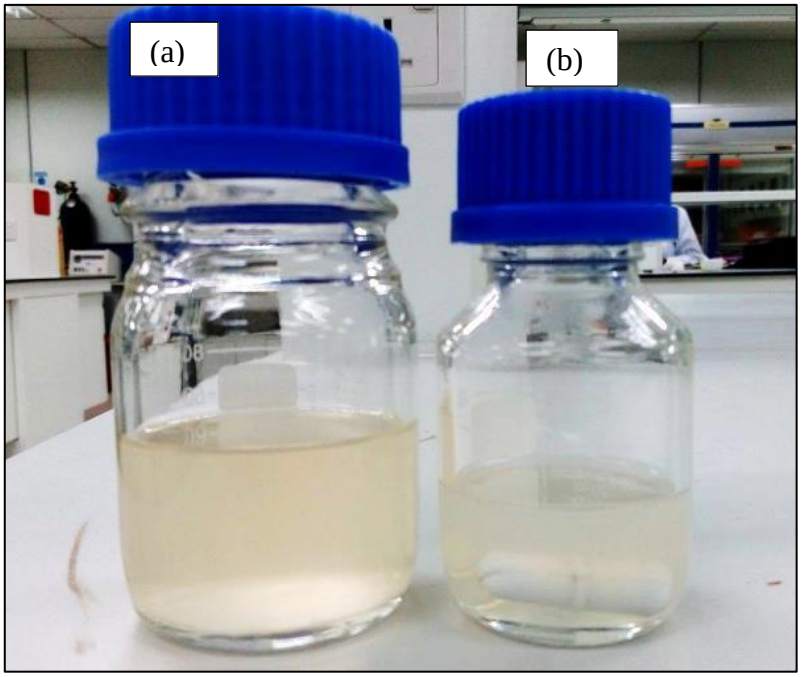

Figure 3.3. (a) Pure ZnO (b) Ag-doped ZnO

3.2.4 Deposition of Pure and Silver Doped Zinc Oxide on Glass Substrate

Spin coating technique was used to deposit the thin films (Figure 3.4). For deposition process, 10 drops of the precursor was deposited onto the centre of the substrate surface by using a disposable dropper. The sample was spun at 3000 rpm for 60 seconds. This process yield a wet film and heat treatment was applied at 80 °C for 10 minute. The purpose of applying heat treatment is to evaporate the solvent and organic residual on the film surface. The process was repeated for 3, 5, 7, 9 and 11 times to obtain the best thickness of thin films (Cui et al., 2013). The process of spin coating is summarized in Figure 3.5.

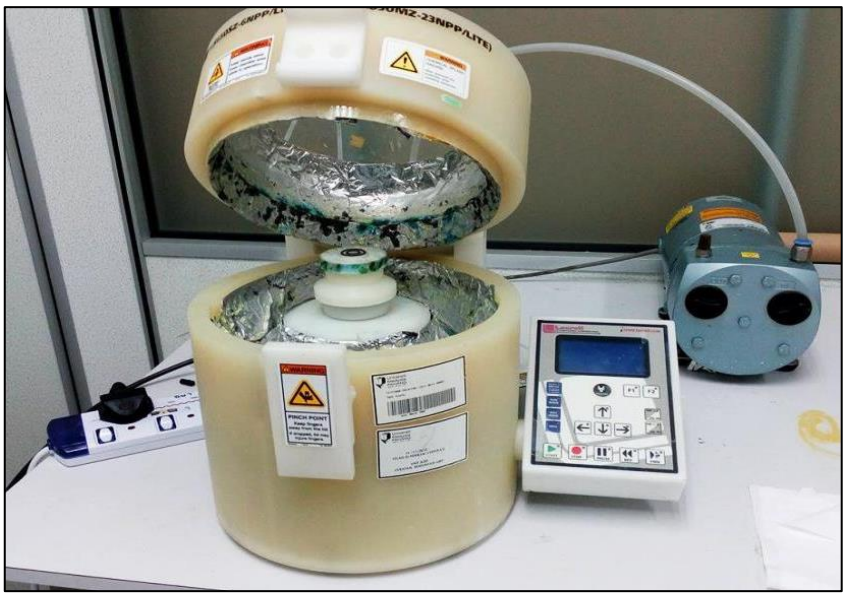

Figure 3.4. Spin coater machine

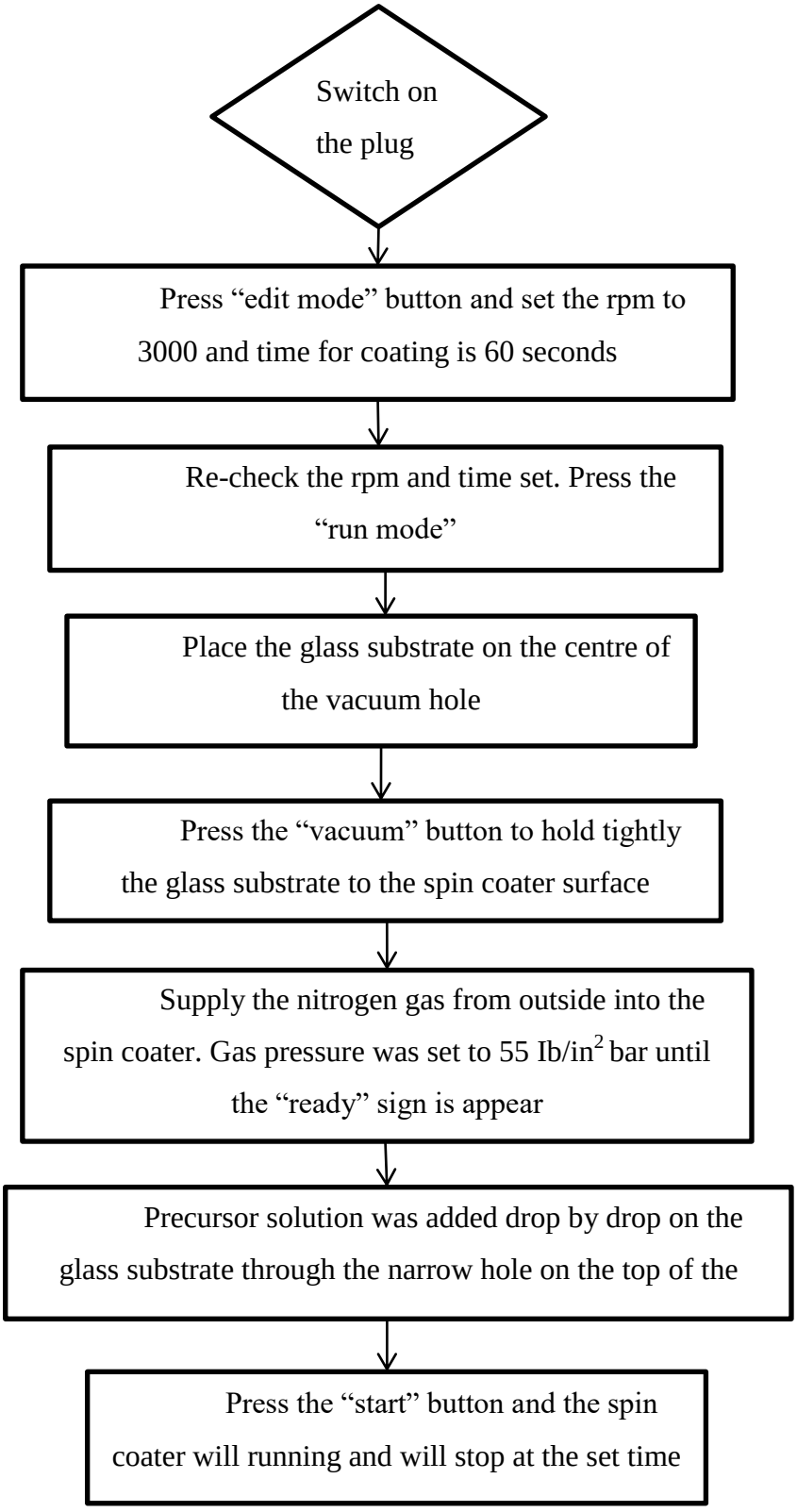

Figure 3.5. Standard operating procedure of spin coating

3.2.5 Annealing Process

Annealing process is the final step to produce dry thin films. The film was inserted in a furnace of 300 °C for 60 minutes and let it cool down in the furnace. After annealing process, the films were placed in a clean petri dish and covered with two layers of parafilm and kept in the dessicator. This method will prevent the films from being oxidised and contaminated. All of the films are ready for characterized.

3.3 MATERIAL CHARACTERIZATIONS

In order to get exact information about the crystal structure, surface morphology, particle size and optical transmission, the following characterization techniques are applicable:

- X-ray Diffraction (XRD)
- UltraViolet-Visible Spectrophotometry (UV-VIS)
- Field Emission Scanning Electron Microscope (FESEM)

3.3.1 X-ray Diffraction (XRD)

X-ray diffraction is a non-destructive analytical technique which can yield the unique fingerprint of Bragg reflections associated with a crystal structure. In this study, the XRD instrument of Rigaku brand comes from model Miniflex II manufactured on October 2011 (Figure 3.6) is used to investigate the orientation and crystal structure of the pure and silver doped zinc oxide thin film with Cu Kα (λ = 0.1542 nm) and the angle 2θ ranged from 20° to 80°. The scan rate used was 1°/min. During the analysis, the current and voltage were maintained at 15 mA and 30 kV respectively.

Figure 3.6. XRD instrument

3.3.2 Field Emission Scanning Electron Microscope (FESEM)

Surface morphology of undoped and silver doped zinc oxide are being observed using Field Emission Scanning Electron Microscope, (FESEM) instrument comes from model JSM-7800F of JEOL USA. At a working distance of 3 mm, FESEM would perform a resolution of 2.5 nm at 2 kV which is low magnitude of voltage which is the greatest advantage of using FESEM. Besides, an elemental mapping can be obtained in just a short time and able to know composition and topography of the specimen via Energy Dispersive X-Ray (EDX) which was attached to the FESEM (Figure 3.7)

Figure 3.7. FESEM-EDX instrument

3.3.3 UltraViolet-Visible Spectrophotometry (UV-VIS)

Instrument that is used to record the absorption spectra and the optical transmittance of the thin films is UV-Vis Spectrophotometer (Figure 3.8). The thin films are prepared under optimized condition and analyzed at the visible range. The wavelength used this this experiment is from 200 nm to 800 nm.

Figure 3.8. UV-Visible instrument

CHAPTER 4

RESULT AND DISCUSSIONS

4.1 INTRODUCTION

This chapter discussed and analysed about all the characterizations of the samples regarding to XRD, UV-Vis and FESEM. The discussion included the plotted graph, images and tabulation of data.

4.1.1 XRD Analysis

Figure 4.1 (a) and (b) shows the XRD spectra of ZnO and SZO prepared by sol-gel method which the prepared precursor was particles deposited on the glass substrate at 3, 5, 7, 9 and 11 layers, respectively. The XRD spectra of ZnO in Figure 4.1 (a) shows the sharp and narrow phase of (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) belongs to polycrystalline hexagonal ZnO crystal structure. The (h k l) peaks of 3 layers increases until it reach maximum intensity at 9 layers of ZnO but the peaks lowered again at 11 layers ZnO. The minimum (h k l) intensity were positioned at 31.74°, 34.31° and 36.18° which is correspond to (1 0 0), (0 0 2) and (1 0 1) phase respectively for 3 layers ZnO. Meanwhile, 9 layers ZnO demonstrating the XRD spectra where the phase is maximum at (1 0 0), (0 0 2) and (1 0 1) located at 2θ of 31.75°, 34.36° and 36.210°, respectively. In this figure, it shows that the dominance phase was at phase of (1 0 1). There is no report on the existence of diffraction pattern corresponding to impurities. It is proved that pure nanoparticles were successfully synthesized.

Figure 4.1 (b) shows the XRD spectra of SZO at various layers. From the figure, it shows that the intensity of ZnO phase increases proportionally with increasing layers of SZO. There is an additional impurities peak were detected indicating the presence of silver, Ag element at phase of (1 1 1) and (2 0 0). Both of this peaks reflected to face centered cubic crystal structure. However only peak (1 1 1) appears clearly in the spectra even the intensity is not too prominent compared to the peak of (2 0 0). This is due to only small amount of doping used in SZO synthesis. From the spectra, it is clearly seen that when the depositions layer increases, the XRD intensity also increases becomes narrower and sharper. It is believed that the larger Ag^{+} ion (1.22Å) which is having higher ionic size compared to Zn^{2+} ion (0.74 Å) had replaced the substitution site of ZnO crystal lattice resulting in increment in the XRD peak. This situation suggesting that the interstitial site of ZnO has been occupied by the Ag ion, and compatible with the report by Ahn et al., (2006)

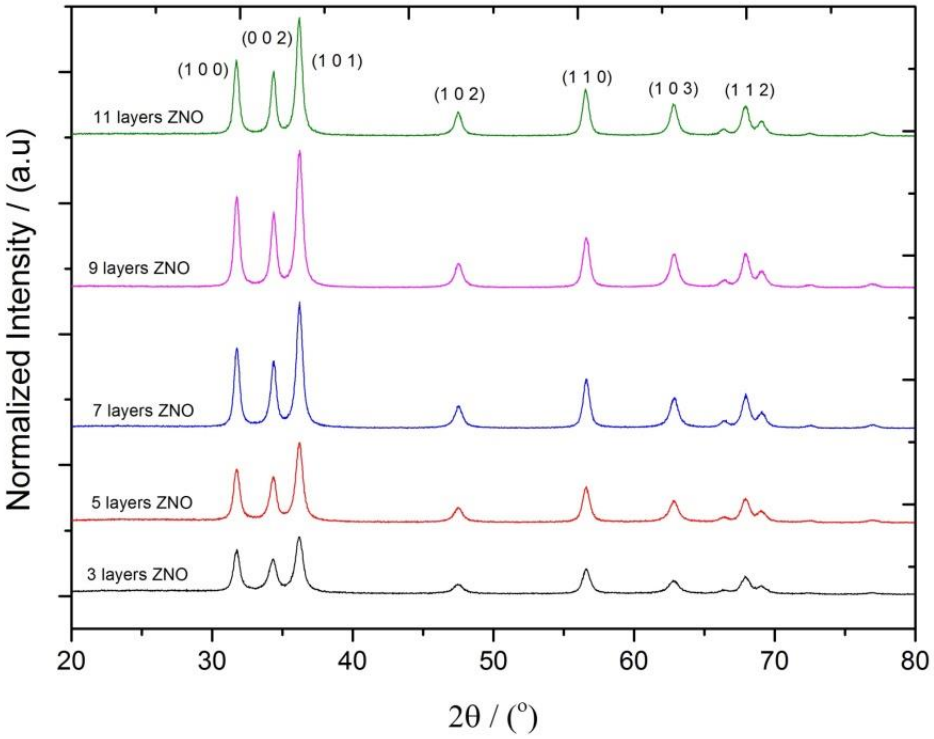

Figure 4.1 (a). XRD spectra of ZnO at 3, 5, 7, 9 and 11 layers

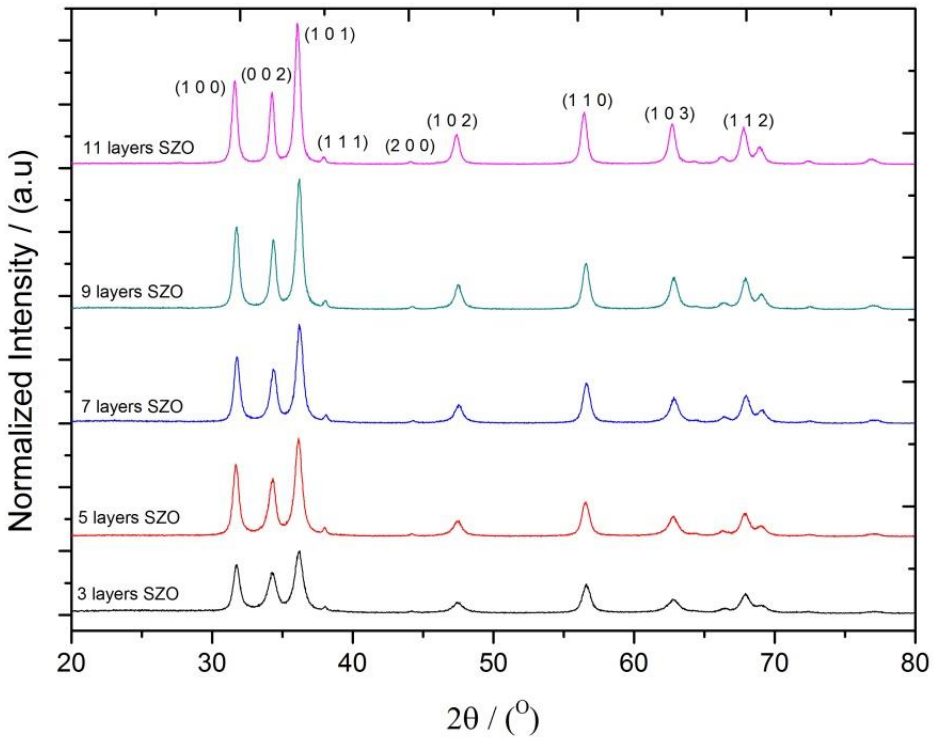

Figure 4.1 (b): XRD spectra of SZO at 3, 5, 7, 9 and 11 layers

Table 4.1 shows that increases in deposition layer for ZnO and SZO would increase the intensity of (1 0 1) phase but full width at half maximum (FWHM) decreases. The same results obtained by Xu et al., (2011). FWHM decreases indicate that the quality of crystalline structure becomes better as the thickness increases.

Table 4.1

FWHM of ZNO and SZO at (1 0 1) phase

(1 0 1) phase	**2θ (O)**	**FWHM (O) ZnO**	**FWHM (O) SZO**
3 layers	36.149	0.622	0.706
5 layers	36.109	0.570	0.611
7 layers	36.205	0.529	0.560
9 layers	36.180	0.520	0.513
11 layers	36.061	0.488	0.446

The crystallite size D of pure ZnO and all sample along the c-axis were calculated according to the Scherrer equation (1):

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \tag{1}$$

where D is the crystallite size, λ is the X-ray wavelength (λ = 1.5406 ˚A), β is the full width at half-maximum (FWHM), and θ is the Bragg angle.

In order to obtain detailed information about the wurtzite structure, the lattice constants a and c were calculate using the formula of (2):

$$\frac{1}{d^2{}_{hkl}} = \frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \tag{2}$$

where (h k l) are the Miller indices of the respective crystalline planes, a = b and c stand for the lattice parameters of the hexagonal ZnO structure and d_{hkl} is the distance between (h k l) planes

Table 4.2 (a) and (b) shows the calculated lattice constant, a and c of ZnO and SZO at phase (1 0 0) and (0 0 2). The standard value of lattice parameter of a and c from JCPDS data (Powder Diffraction File, Card no: 36-1451) are 3.252 Å and 5.215 Å (Nanda Shakti et al., 2010). The standard value for hexagonal cell c/a = 1.633. From the data that had been tabulated on the Table 4.2, value of lattice constant a and c were compatible with the standard value while value of c/a proved that the synthesized ZnO ans SZO were matched ideally with hexagonal wurtzite structure.

Table 4.2 (a)

Calculated lattice constant, a and c of ZnO at phase (1 0 0) and (0 0 2)

Sample	**d at (1 0 0) (Å)**	**d at (0 0 2) (Å)**	**a (Å)**	**c (Å)**	**c/a**
3 layers	2.817	2.612	3.253	5.224	1.606
5 layers	2.817	2.608	3.253	5.216	1.603
7 layers	2.815	2.605	3.250	5.210	1.603
9 layers	2.816	2.608	3.252	5.216	1.604
11 layers	2.817	2.606	3.253	5.212	1.602

Table 4.2 (b)

Calculated lattice constant, a and c of SZO at phase (1 0 0) and (0 0 2)

Sample	**d at (1 0 0) (Å)**	**d at (0 0 2) (Å)**	**a (Å)**	**c (Å)**	**c/a**
3 layers	2.816	2.615	3.252	5.230	1.608
5 layers	2.820	2.610	3.256	5.220	1.603
7 layers	2.816	2.605	3.252	5.210	1.602
9 layers	2.817	2.608	3.253	5.216	1.603
11 layers	2.828	2.614	3.265	5.228	1.601

4.1.2 Optical Analysis

Figure 4.2 (a) shows the graph of transmittance against wavelength spectra of pure ZnO thin films. From the graph, it is revealed that ZnO thin films having good optical transmittance of above 80 % in the visible range (380 – 780 nm). It is clearly seen that the least layer of film yield in the highest optical transmittance while the films of 11 layers of deposition having the lowest transmittance.

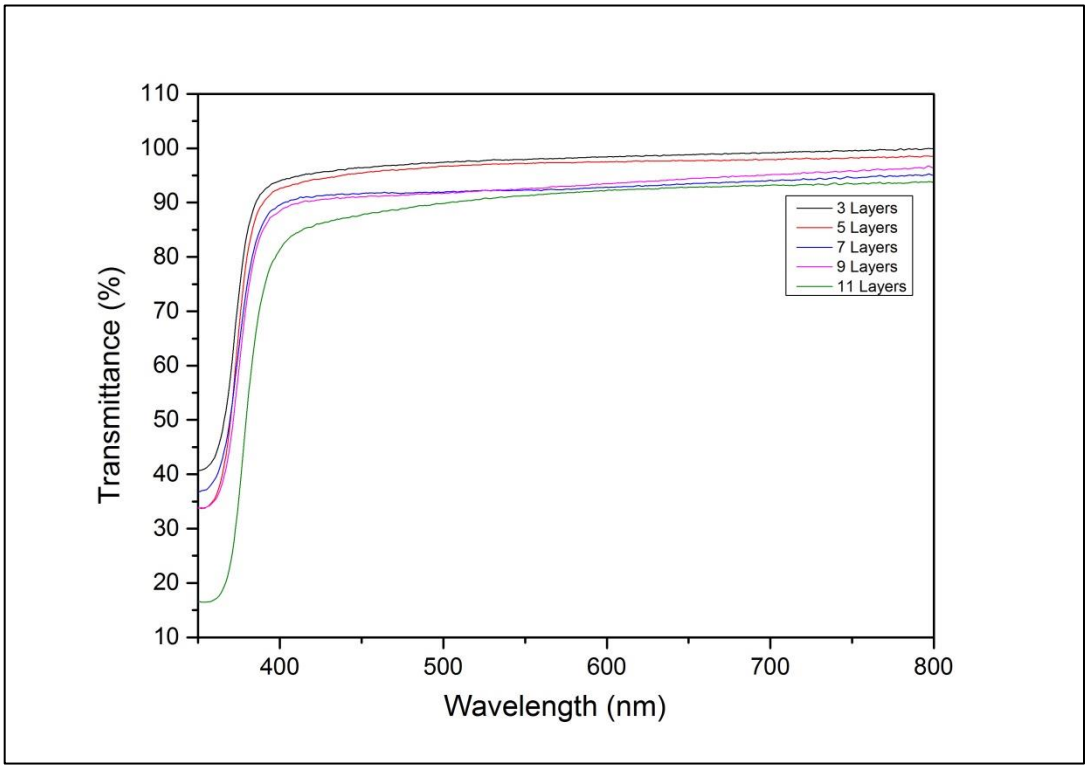

Figure 4.2 (a). UV–visible transmittance spectrum of pure ZnO thin films of 5 different layers

On the other hand, the spectra of SZO exhibit better optical transmittance which is above 90 % in the visible region (Figure 4.2 (b)). This has lead to valuable findings since only small amount of doping used could improve the film transmittance. For 3 layers film, there are sharp fundamental absorption edge was observed at around 390 nm. It was found that 7 layers film have lowest transmittance. The high optical transmittance of the investigated SZO film in the visible light region is attributed to the high transmittance near the infrared regions.

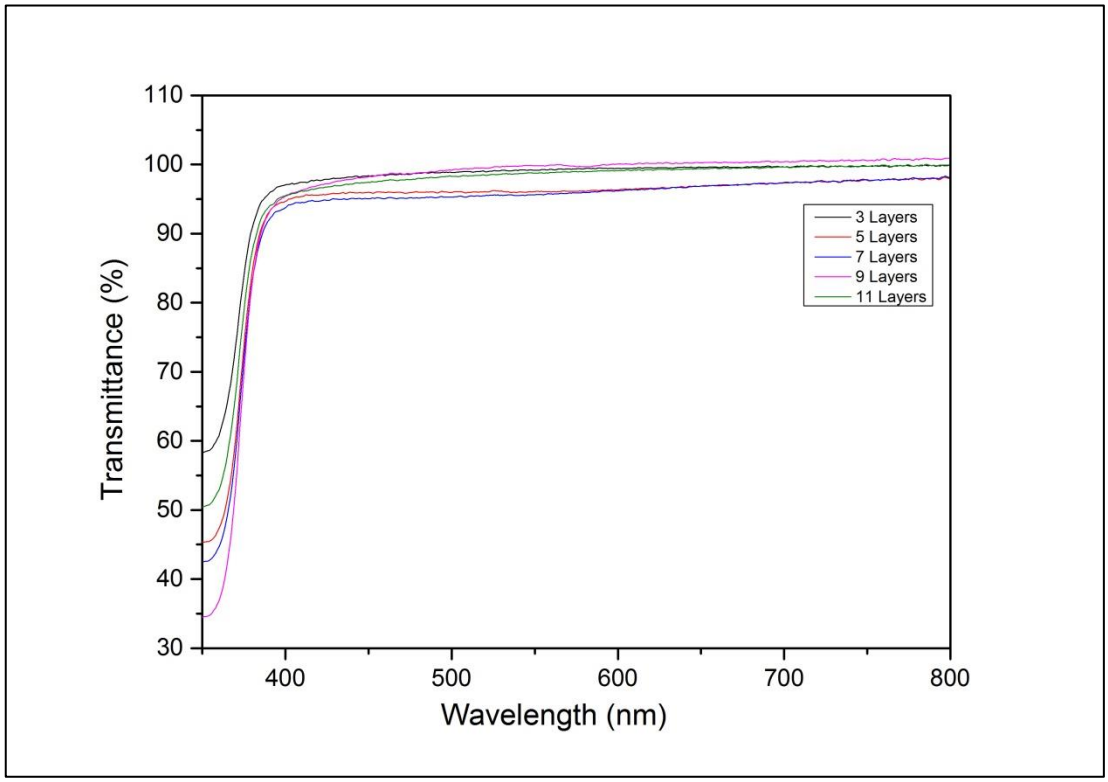

Figure 4.2 (b). UV–visible transmittance spectrum of SZO thin films of 5 different layers

4.1.3 FESEM Analysis

Morphological study of pure ZnO and silver doped zinc oxide, SZO thin films has been investigated using FESEM imaging. Figure 4.3 (a) to (c) presents the imaging of 3 layers of ZnO at 30000, 50000 and 100000 magnification. The grain size of ZnO nanoparticles at 3 layers of deposition varied from 50 nm to 90 nm. The average grain size of the ZnO thin film was calculated via a FESEM software which is approximately 65.43 nm. The particle is having a spherical shape with even distribution. The even distribution of the particles were obtained since high rate of spin coating is applied, which is at 3000 rpm and minimum of 3 layers of deposition is used.

Figure 4.3 (d) to (f) shows the FESEM imaging of 11 layers SZO deposited on the glass substrate at 30000 and 50000 magnifications. It is clearly seen that the grain tend to agglomerate and forms the chromosome-like shape due to thick layers of thin film used which is 11 layers. From the image, several spot of white-spherical particles which are believed that was silver particle can be observed.

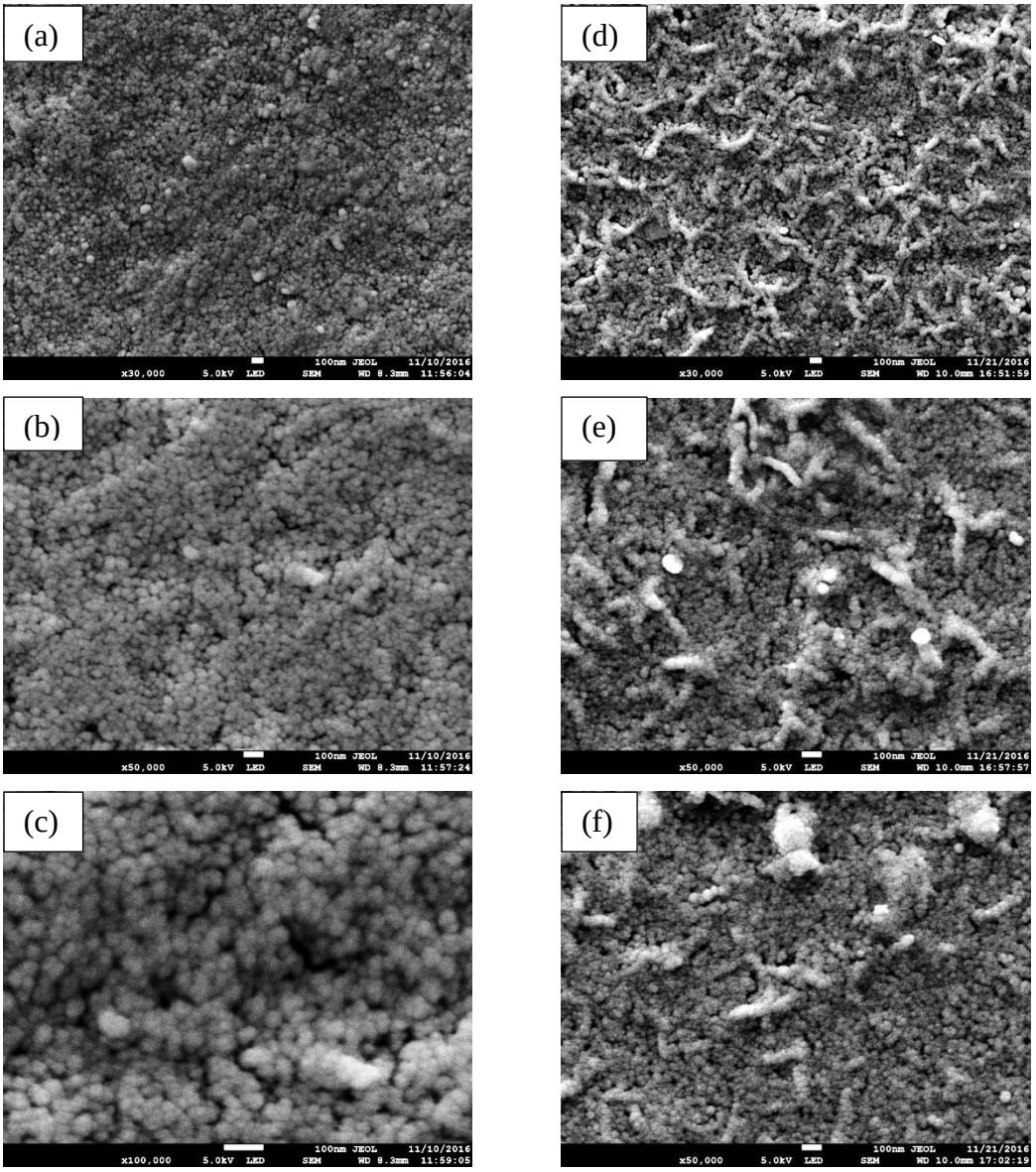

Figure 4.3. (a) to (c) FESEM micrograph of ZnO at 3 layers and (d) to (e) SZO at 11 layers.

Energy dispersive X-ray spectroscopy (EDX)

Figure 4.4 (a) shows the EDX spectra of the ZnO thin films and Table 4.3 (a) show the tabulation data from the EDX spectrum. It is clearly indicated that the existence of pure ZNO in the synthesized ZNO where oxygen and zinc atomic percent is 75.53 % and 24.47 %, respectively.

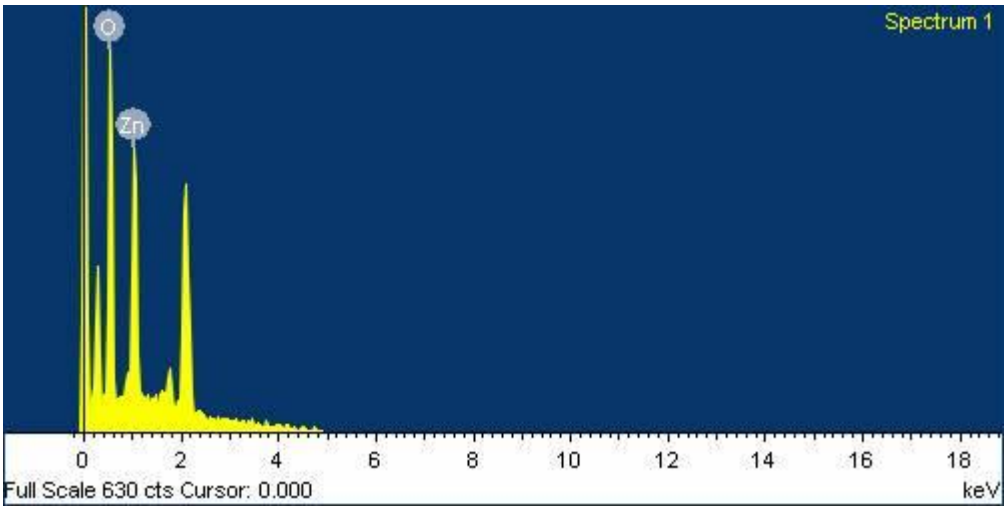

Figure 4.4 (a). EDX pattern of ZnO thin film

Table 4.3 (a)

Tabulation of data from EDX spectra of ZnO thin films

Element	**Weight %**	**Atomic %**
O K	43.04	75.53
Zn L	56.96	24.47
Totals	100	100

In addition, an EDX spectrum of SZO thin film was presented in the Figure 4.4 (b) and the tabulation of data is showed in Table 4.3 (b). Only element of Zn, O and Ag appears in the spectra indicating that there is no other impurity involved in thin sample. Zn, O and Ag contained is 39.12, 60.53, and 0.35 atomic percent respectively. Ag have the least atomic percent since the doping amount used was really in small amount, which is 10 drops.

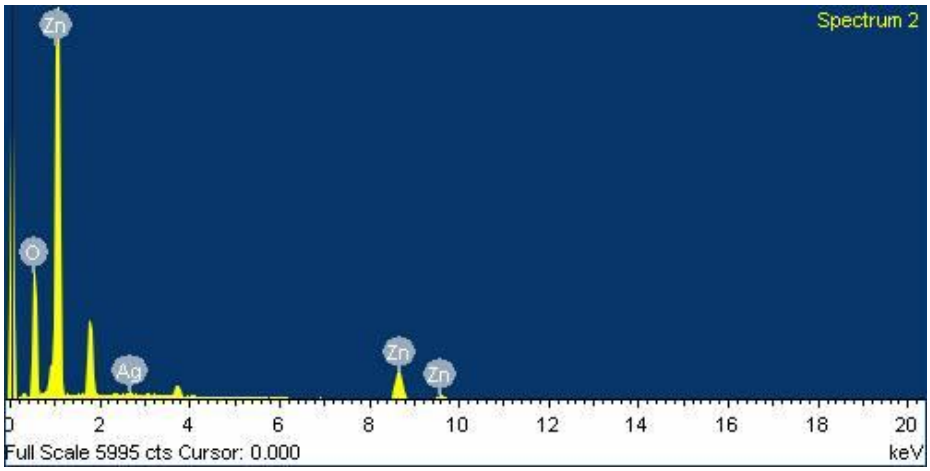

Figure 4.4 (b). EDX pattern of SZO thin film

Table 4.3 (b)

Tabulation of data from EDX spectra of SZO thin films

Element	**Weight %**	**Atomic %**
O K	27.18	60.53
Zn L	71.77	39.12
Ag L	1.05	0.35
Totals	100	100

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

In conclusion, this project has demonstrated the sol-gel synthesis of pure zinc oxide and silver doped zinc oxide followed by the spin coating technique. Zinc acetate dehydrate, isopropyl alcohol, diethanolamine and silver nitrate act as starting material, solvent, stabilizer and source of doping, respectively. The films were deposited on the glass substrate at various layers. An XRD spectrum shows the films crystallinity increases with increasing number of deposition layers without changing the nature wurtzite hexagonal structure of the zinc oxide. Doping of silver shows the existence of (1 1 1) and (0 0 2) peaks indicating the silver element. Lattice constant, c of zinc oxide and silver is compatible with the standard value. The UV-Visible analysis shows the percentage of transmittance are highly influenced by the thickness of thin films. On the other hand, the small amount of Ag doping could increase the transmittance of the films and provide better optical properties. FESEM analysis shows that the 11 layers of thin film having tendency to agglomerate and the EDX spectra proved that the pure ZnO and SZO are successfully synthesize by the sol-gel method.

5.2 RECOMMENDATION

First and foremost, it is highly recommended that atomic-force microscopy (AFM) is used to study the surface morphology of the spin coated ZnO and SZO thin films. By using AFM, we can obtain the three-dimensional (3D) images analysis of the sample and focusing on the surface texture and roughness, grain size and distribution of the atoms.

In this study, there was a problem occurred obtain the get the good sample of thin film to be characterized for XRD. The problem was due to the film thickness which is too thin as no peaks were detected by the XRD instrument. It is believed that the other factor contributed is due to the short aging time which is only 30 minutes. Aging time seems to be one of the important factors to ensure a well-interconnected sol-gel network is build before spin coating technique is applied. Hence, is suggested the precursor solution must be ages for 24 hour or more to obtain the good results. Besides, to get a good thickness of the thin films, the deposition layer should be increased. It is suggested to deposit the films with greater layer, for example 15 layers and above.

Once the desired thickness of thin films was obtained, measuring the thickness would be such a compulsory. Therefore, it is suggested to use ellipsometer instrument or atomic force microscopy (AFM).

Another recommendation, for the upcoming research, it is suggested to use non-toxic and eco-friendly material as stabilizing agent. From the previous study, it is stated that epigallocatechin gallate (EGCG) contained in coffee beans, green tea and the other natural sources would works as capping agent and offers numerous advantages of eco friendliness and compatibility for pharmaceutical and other biomedical applications.

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