

CHAPTER 4

EXPERIMENTAL PROCEDURE

This chapter describes the experimental procedures which involve a brief description of the techniques for each process, e.g. synthesis of ZnO(Al) target, substrate preparation, fabrication of ZnO(Al) thin films and characterization of ZnO(Al) thin films.

4.1 Synthesis of ZnO(Al) Targets

In this thesis, we prepared targets with different weight percent (wt%) of Zn in the target: 0 {ZnO(Al)}, 1, 3 and 6 wt% of Zn embedded in ZnO(Al).

4.1.1 ZnO(Al) Target

The ZnO(Al) target was prepared from ZnO powder (Alfa Aesar, purity of 99.999%) and Al₂O₃ powder (Alfa Aesar, purity of 99.99%). The preparation process of ZnO(Al) can be described as the followings:

(1) Preparation of composition and mixing processes

ZnO powder and Al₂O₃ powder was baked in a furnace at a temperature of 900 °C about 3 hours to eliminate the moisture in the powder and to make sure that the powder is perfect oxide compound. In order to have a ZnO target with Al₂O₃ 2.5 wt%, 97.5 g of ZnO powder and 2.5 g of Al₂O₃ powder were mixed by a sieve, ground in a mortar, and then rolled by a lathe at a speed of 55 RPM for 1 hour.

(2) Pressing the target

The obtained mixture was sprayed by deionized water until the mixture had just enough uniform moisture. Less moisture may cause cracks in the target after pressing. On the other hand, too much moisture in the powder results in the difficulty in pressing. The mixture was then put into a mold of which the diameter is 2 inches. It

was pressed under a pressure of 5–5.5 tons per square inch in air at room temperature and hold at that pressure for 50 mins. For the composition of mass mentioned in step (1), we obtained a 2-inch in diameter pellet with 6 mm thick. Next, the target was removed from the mold and placed in the chamber under humidity control for about 24 hours.

(3) Sintering the target

The ZnO pellet was baked at a temperature of 120°C about 2 hours. After that the pellet was sintered at 1050°C for 3 hours in the air atmosphere. The temperature profile during the sintering process is shown in Fig. 4.1. The temperature was gradually ramped up to 1050°C in about 6 hours and stayed at that temperature for 3 hours before the power was completely shutdown, as seen in Fig 4.1. The temperature of furnace was freely cooled down toward the room temperature. The obtained ZnO(Al) target looks like a white ceramic target having a rough surface.

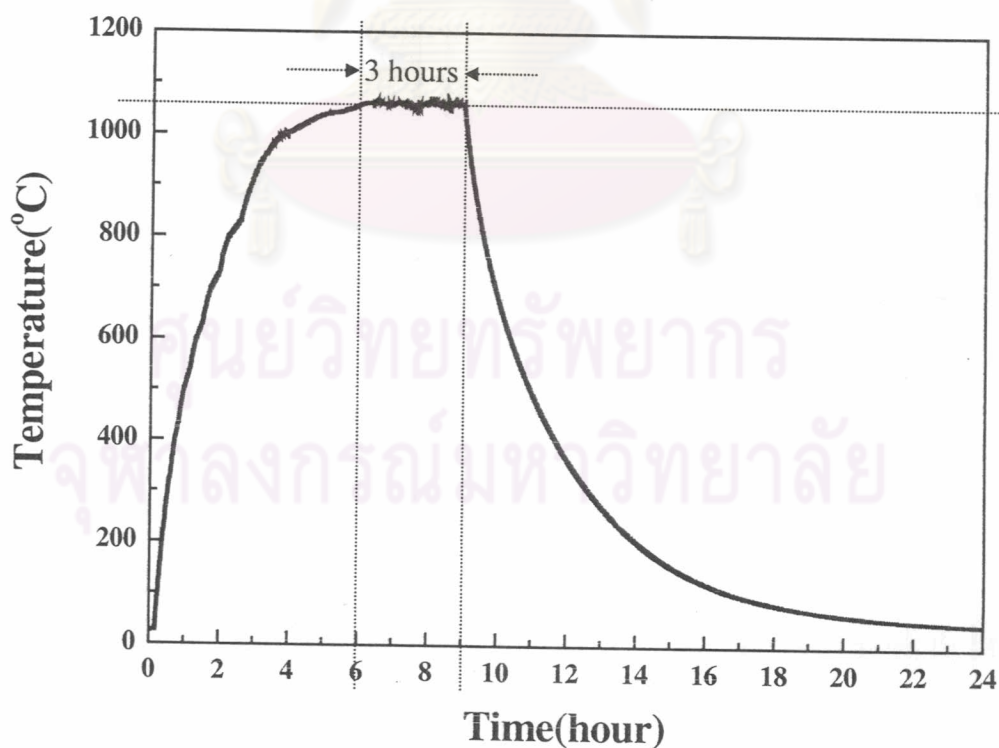


Figure 4.1: The temperature profile during sintering of ZnO(Al) target.

In order to install the target in the sputtering system, the thickness of the target must be reached to about 5 mm. thick to fit into the sputtering gun. To achieve this requirement, the target had to be polished down.

4.1.2 Embedded-Zn ZnO(Al) Target

In order to prepare Zn embedded in the ZnO(Al) target with varying Zn contents of 1, 3 and 6 wt%, the preparation process in section 4.1.1 was used and added 1, 3 and 6 g of pure Zn (Alfa Aesar, purity of 99.999%), respectively, into the mixture. By repeating the second and the third processes in section 4.1.1, we obtained the embedded-Zn ZnO(Al) targets. The obtained target was the white ceramic target with black Zn metal scattered in the target as schematically shown in Fig. 4.2 (b). For more Zn content, the distribution of Zn in the target is more noticeable.

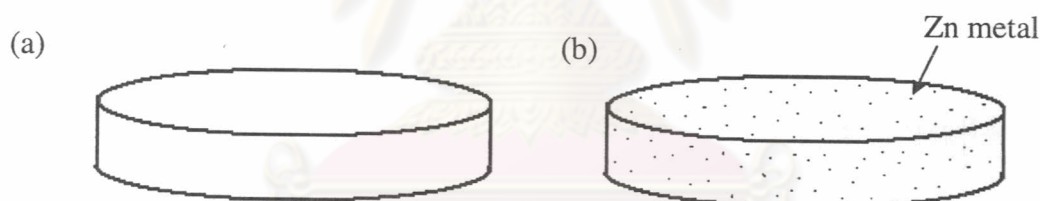


Figure 4.2: (a) ZnO(Al) target, (b) Embedded-Zn ZnO(Al) target. Black spots represent Zn metals.

Table 4.1: The properties of ZnO(Al) targets

target	Al ₂ O ₃ (wt%)	Zn (wt%)	Density (g/cm ³)
ZnO(Al) 0 wt%	2.5	0	3.34
ZnO(Al) 1 wt%	2.5	1	3.48
ZnO(Al) 3 wt%	2.5	3	3.45
ZnO(Al) 6 wt%	2.5	6	3.50

Table 4.1 summarizes the properties of ZnO(Al) targets. In this thesis, we prepared four different targets by varying Zn contents of 0, 1, 3 and 6 wt% adding to the ZnO(Al) target. The densities of the targets are in the range 3.34–3.50 g/cm³.

4.2 Substrate Preparation

Soda–lime glasses (SLG) of 4.85 × 5.85 cm² in area and thickness of 2 mm were used as substrates for deposition of ZnO(Al) thin films. The substrates were cleaned with household detergent to remove coarse dust particles and next ultrasonically cleaned in deionize water mixed with detergent for 15 mins. Then the substrates were ultrasonically cleaned again in only deionize water for 15 mins twice and dried in flowing nitrogen gas. The substrates were soaked in chromic acid (KCr₂O₄ + H₂SO₄) about 12–24 hours. After that, the substrates were ultrasonically cleaned again in deionize water for 15 mins. Finally the substrates were dried in flowing nitrogen gas and baked at 120 °C for 1 hour before they were loaded in the sputtering system for thin film deposition.

4.3 Fabrication of ZnO(Al) Thin Films

The ZnO(Al) target was installed on the sputtering gun with thin silver paste applied between the target surface and the gun surface. The silver paste is used to bring the heat generated during the sputtering process out of the target to the cooling system. Figure 4.3 shows a schematic diagram of the RF magnetron sputtering system used in this work. The ZnO(Al) thin films were deposited by RF magnetron sputtering on soda–lime glass substrates. The substrates were fixed on a holder parallel to the target surface with the substrate–target distance of 6.5 cm. Our holder can accept up to 4 substrates at a time. The shutter was placed between the target and the substrates to prohibit undesired sputtered atoms during pre–sputtering process. During the deposition, the substrates holder can be rotated. This configuration of sputtering process is called the planar sputtering.

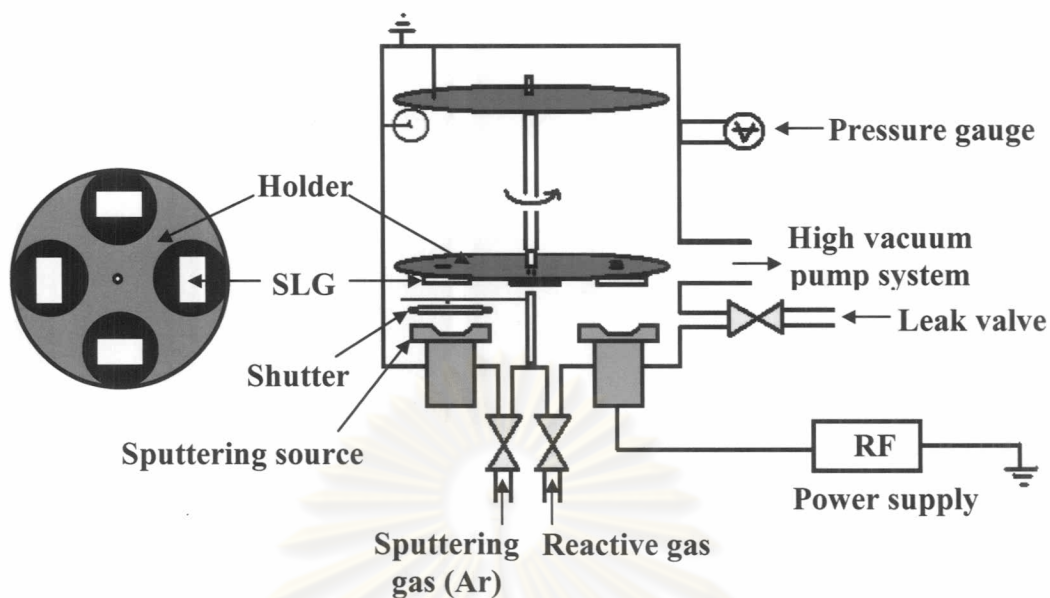


Figure 4.3: The schematic diagram of RF magnetron sputtering system.

After installing the target and the substrates in the vacuum chamber, a turbo molecular pump and a roughing pump were used to evacuate the chamber to obtain high vacuum (in the order of 10^{-6} mbar). Before using target, we generally sputtered the target with the RF power of 100 W at argon gas pressure of 8.0×10^{-3} mbar for about 20 mins to clean the target surface. Before the deposition in each condition of sputtering was started, the chamber was evacuated to a base pressure below 5.5×10^{-6} mbar. The target surface must be improved by sputtering of 3 min at an oxygen gas pressure of 4% (3.2×10^{-3} mbar) of sputtering gas pressure, which was 8.0×10^{-3} mbar and RF power of 100 W. After the target surface was improved, its surface shows white coloration due to oxygen atoms diffused into the surface, resulting in more perfect ZnO structure in the target.

The chamber was then evacuated to the base pressure below 5.5×10^{-6} mbar again and refilled with argon gas at the required working gas pressure. These processes (evacuation–refill) were repeated three times to dilute other gas species. Next, the target was pre-sputtered before the deposition of the films at the required RF power for 5 mins. The deposition was divided into intervals, each interval for 20–25 mins. This is because during the deposition, the positive ions knocked on the target surface and generated heat at the target. The heat was transferred into the sputtering gun, which could deteriorate the magnet in the sputtering gun.

Table 4.2: The sputtering parameters of deposition for ZnO(Al) films by RF magnetron sputtering.

Base pressure	5.5×10^{-6} mbar
RF power	50 – 125 W
Argon gas pressure	6.0×10^{-3} – 1.0×10^{-2} mbar
Target – to – substrate distance	6.5 cm
Substrate temperature	not intentionally heated
Embedded–Zn ZnO(Al) targets	0 – 6 wt% (Zn content)

The deposition parameters for the ZnO(Al) films are summarized in Table 4.2. According to Table 4.2, ZnO(Al) films were deposited at various RF powers; 50, 75, 100 and 125 W, with fixed argon gas pressure to examine the effect of the RF power on the properties of the films. In the same way, various argon gas pressure; 6.0×10^{-3} , 8.0×10^{-3} and 1.0×10^{-2} mbar at fixed RF power were used to examine the influence of the argon gas pressure on the properties of the films. Similarly, various additional Zn contents; 0, 1, 3 and 6 wt% deposited at the same RF power and argon gas pressure were used to examine effect of Zn content (wt%) on the properties of films.

4.4 Characterization of ZnO(Al) Thin Films

4.4.1 Optical Characterization

– Transmission Spectra

The transmission spectra of films can be used to determine the film thickness, the absorption coefficient and the energy gap of the films. In this thesis, the transmission spectra of the films in the ultraviolet–visible–near infrared (UV–Vis–NIR) region were measured by using the Perkin Elmer model Lambda 900 double–beam spectrometer in the wavelength range 300–1500 nm. The schematic diagram of spectrometer is shown in Fig. 4.4.

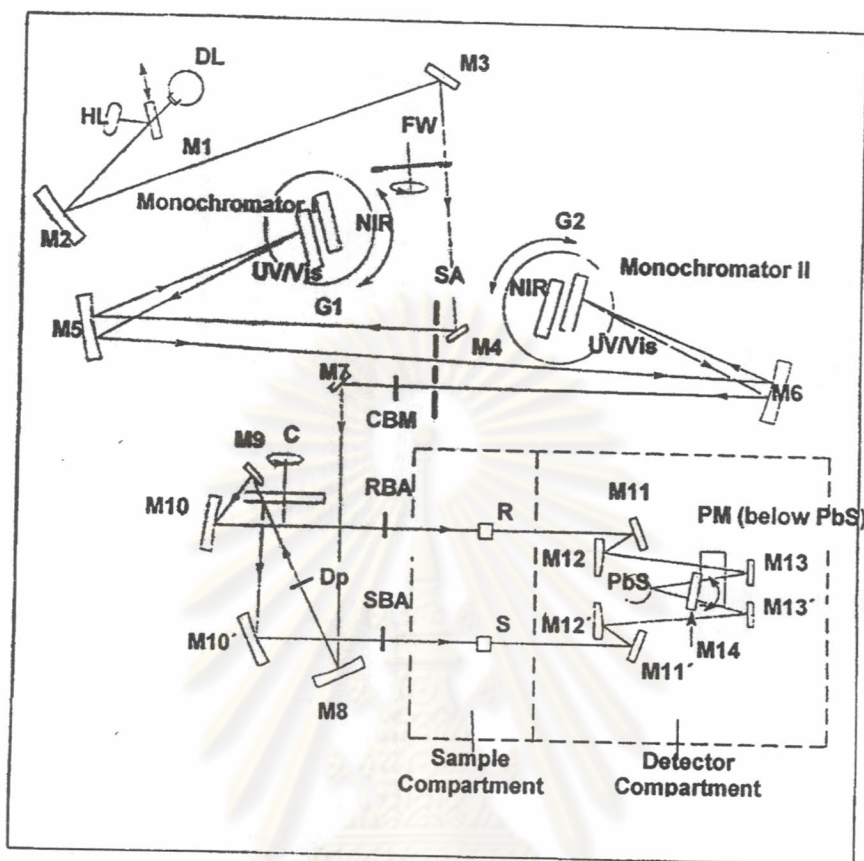


Figure 4.4: Schematic diagram of spectrometer.

There are two radiation sources, a deuterium lamp (DL) and a halogen lamp (HL), covering the working wavelength range of the spectrometer. For operation in the near infrared (NIR) and visible (Vis) ranges, source mirror M1 reflects the radiation from the halogen lamp onto mirror M2. At the same time it blocks the radiation from the deuterium lamp. For operation in the ultraviolet (UV) range, mirror M1 is raised to permit radiation from the deuterium lamp to mirror M2. Radiation from the respective source lamp is reflected from mirror M2 via mirror M3 through an optical filter on the filter wheel assembly (FW) to mirror M4. The filter wheel is driven by a stepping motor to be in synchronization with the monochromators. From mirror M4 the radiation is reflected through the entrance slit of monochromator I. All slit are located on the slit assembly (SA). The radiation is collimated at mirror M5 and reflected to the grating table G1. The radiation is dispersed at the grating to produce a spectrum and reflected to mirror M5 then through the exit slit. The exit slit of

monochromator I serves as the entrance slit of monochromator II. The radiation is reflected via mirror M6 to the appropriate grating on grating table G2 and then backs via mirror M6 through the exit slit to mirror M7. From mirror M7 the radiation beam is reflected via mirror M8 to the chopper assembly (C). As the chopper rotates, a mirror segment, a window segment and two dark segments are brought alternately in to the radiation beam. When a window segment enters the beam, radiation passes to the mirror M9 and is then reflected via mirror M10 to create the reference beam (R). When a mirror segment enters the beam the radiation is reflected via mirror M10' to create the sample beam (S). At the part of sample compartment (see Fig. 4.4), the soda-lime glass was placed at position reference (R). The transmitted beam from soda-lime glass is used for reference beam because ZnO(Al) thin films (sample) was deposited on one side of soda-lime glass. The radiation passing alternately through the sample and reference beams is reflected by mirror M11, M12, M13 and M11', M12', M13', respectively of the optics in the detector assembly onto the appropriate detector. Mirror M14 is rotated to select the required detector. A photo multiplier (PM) is used in UV/Vis range while a lead sulfide (PbS) detector is used in the NIR range.

The transmission were measured in percent of the ratio of intensity of the sample beam to intensity of the reference beam, which transmitted through the sample and the soda-lime glass, respectively, as shown in Fig. 4.5. The transmission, T is defined as

$$T = \frac{I_t}{I_0}, \quad (4.1)$$

where I_0 is the reference beam intensity and I_t is the intensity of the beam passing through the sample.

Generally, the transmission spectra of the semiconductors films can be divided into two distinct wavelength regions. At long wavelengths (photon energies less than the energy gap), T exhibits oscillation from interference effects in the transparent films. At short wavelengths (photon energies greater than energy gap), T rapidly decreases to zero. Such a typical transmission characteristic is presented in Fig. 4.6.

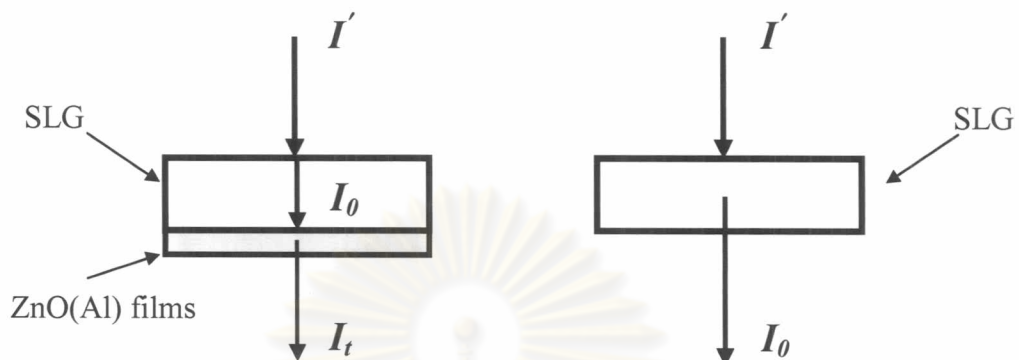


Figure 4.5: Schematic of optical transmission measurement.

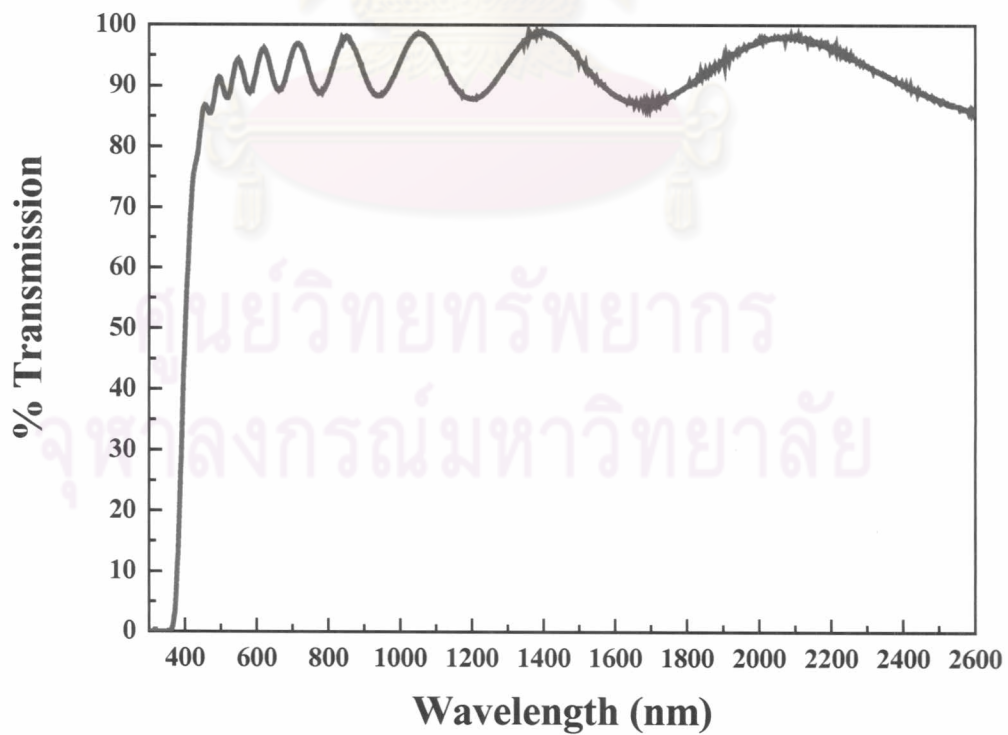


Figure 4.6: Transmission spectra of ZnO thin films.

– Thin Film Thickness

From the transmission spectra, the films thickness d can easily be determined from the formula [30]

$$d = \frac{N_{\text{cyc}} \lambda_1 \lambda_2}{2|n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1|}, \quad (4.2)$$

where N_{cyc} is number of cycles observed from wavelength λ_1 to λ_2 ($\lambda_1 < \lambda_2$) and $n(\lambda_1)$, $n(\lambda_2)$ are refractive indices of λ_1 and λ_2 , respectively.

Assuming that $n(\lambda_1) \approx n(\lambda_2)$ for the two adjacent maxima (or minima), then $N_{\text{cyc}} = 1$, the Eq. 4.2 can be written as

$$d = \frac{\lambda_1 \lambda_2}{2n|\lambda_1 - \lambda_2|}, \quad (4.3)$$

In this thesis, the refractive index of ZnO(Al) thin films is taken to be 2.02 [4].

– The Absorption Coefficient

Generally, the transmission intensity I of radiation wave through the films of thickness d can be written as

$$I = I_0 \exp(-\alpha d),$$

where α is the absorption coefficient. From Eq. 4.1, we obtain

$$\alpha = \frac{1}{d} \ln \left(\frac{100}{\%T} \right). \quad (4.4)$$

– **The Energy Gap, E_g**

In the direct gap semiconductors, α and optical energy gap (E_g) are related by

$$\alpha h\nu = A(h\nu - E_g)^{1/2},$$

or

$$(\alpha h\nu)^2 = A^2(h\nu - E_g), \quad (4.5)$$

where A is a constant, h is the Planck's constant and ν is the frequency of the incident radiation. The energy gap can be obtained by extrapolating the linear part of the resulting curve from Eq. 4.5.

Figure 4.7 is an example plot of $(\alpha h\nu)^2$ versus $h\nu$ of ZnO films. The linear dependence of $(\alpha h\nu)^2$ to $h\nu$ indicates that films are the direct transition-type semiconductor [13]. The photon energy at the point where $(\alpha h\nu)^2$ is zero is the energy gap.

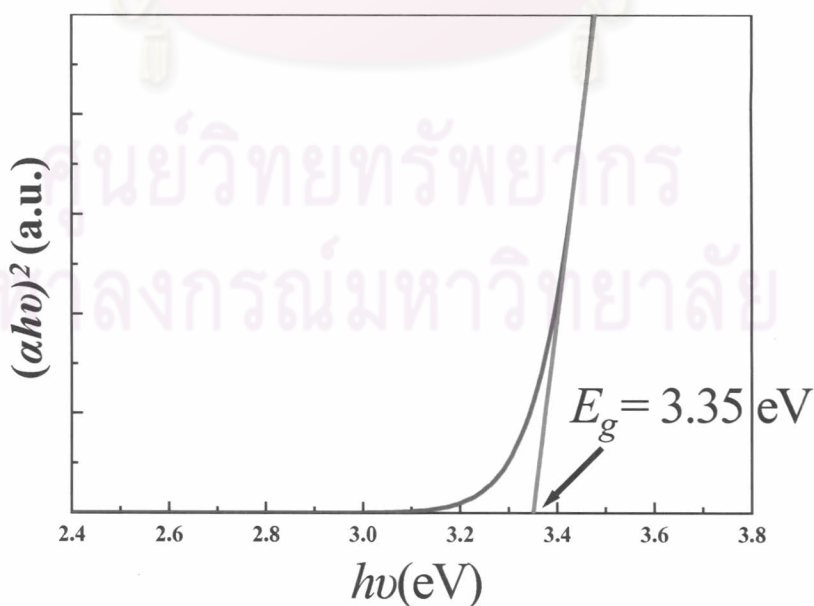


Figure 4.7: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for ZnO films.

4.4.2 Electrical Characterization

In this thesis, the electrical properties such as electrical resistivity, Hall mobility and carrier concentration were obtained by a computerized Hall effect measurement system [34]. Figure 4.8 shows a schematic set-up of the computerized Hall effect measurement system. This system measures electrical properties by mean of Hall measurement in conjunction with the Van der Pauw technique, which is the four-point probes measurement. The corners of the film surface were made contact with the copper wires using silver paste as the binder. Each contact was labelled with the number 0 to 3 (see Fig. 4.9 (a)). To measure the electrical resistivity, the control system applied the high-voltage constant current to the two electrical contacts on sample and measures the voltage for all possible configuration of the measurement. Note that during the measurement of the electrical resistivity the magnetic field was turned off. For the Hall mobility measurement, the magnetic field was applied in the direction of forward, $+\vec{B}$, (see Fig. 4.9 (b)) and reverse, $-\vec{B}$, (see Fig. 4.9 (c)). The forward and reverse magnetic fields were controlled by the magnet controller

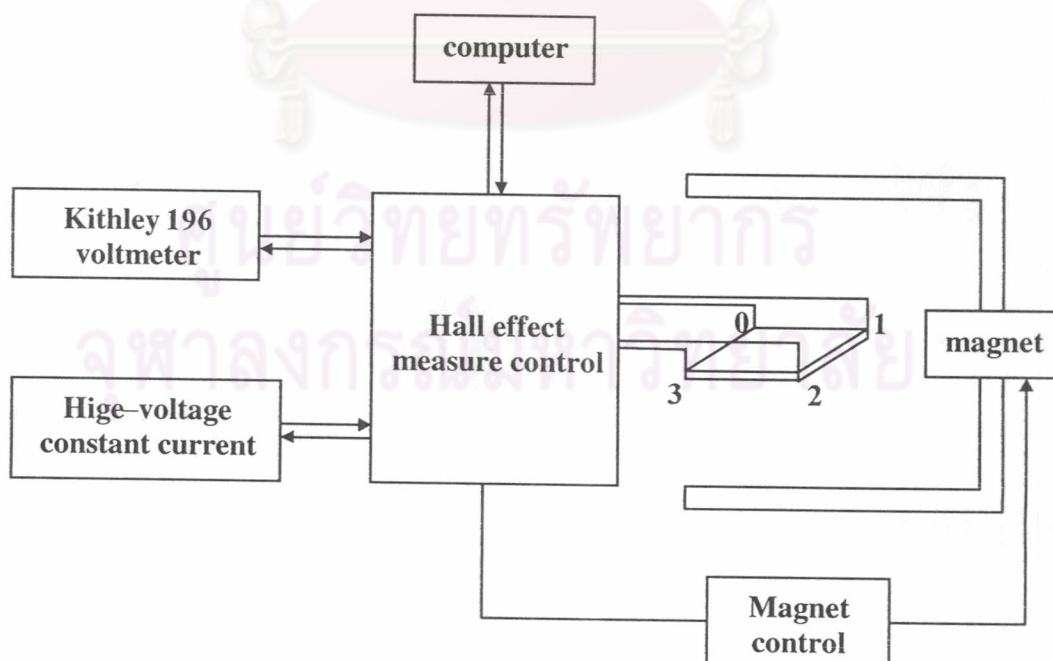


Figure 4.8: Schematic set-up of Hall measurement system.

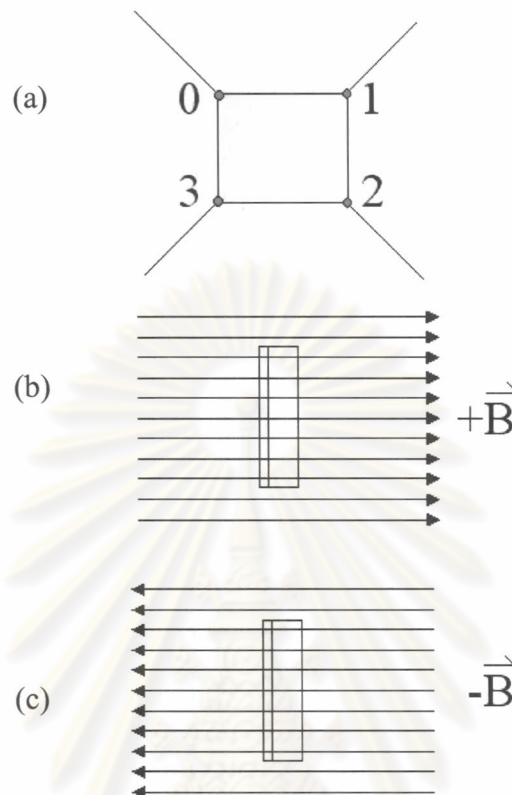


Figure 4.9: The Hall measurement using the Van der Pauw method, (a) each contact was label with number 0 to 3, (b) Hall mobility measurement with applied magnetic field in the forward direction, (c) Hall mobility measurement with applied magnetic field in the reverse direction.

The measurements were taken in 20 configurations as shown in Tables 4.3, 4.4, 4.5 and 4.6. The resistivity was calculated from the measurement in configurations 1–8 (see Table 4.3). The Hall mobility was calculated from the measurement in configurations 13–20 (see Tables 4.5 and 4.6). The configurations 9–12 (see Table 4.4) were used to check the type of semiconductor (n-type or p-type) by comparing the voltage in configurations 13–16 and configurations 17–20 as shown in Table 4.7. The resistivity can be determined from Eq. 3.13. The Hall mobility and carrier concentration can be obtained from Eqs. 3.27 and 3.8, respectively.

Table 4.3: Configurations for electrical resistivity measurement.

Configuration	Measurement parameter	I+	I-	V+	V-
1	I_{12}, V_{30}	I_1	I_2	V_3	V_0
2	I_{21}, V_{30}	I_2	I_1	V_3	V_0
3	I_{23}, V_{01}	I_2	I_3	V_0	V_1
4	I_{32}, V_{01}	I_3	I_2	V_0	V_1
5	I_{30}, V_{12}	I_3	I_0	V_1	V_2
6	I_{03}, V_{12}	I_0	I_3	V_1	V_2
7	I_{01}, V_{23}	I_0	I_1	V_2	V_3
8	I_{10}, V_{23}	I_1	I_0	V_2	V_3

Table 4.4: Configurations for Hall mobility measurement without applied magnetic field through the sample.

Configuration	Measurement parameter	I+	I-	V+	V-
9	I_{13}, V_{20}	I_1	I_3	V_2	V_0
10	I_{31}, V_{20}	I_3	I_1	V_2	V_0
11	I_{20}, V_{13}	I_2	I_0	V_1	V_3
12	I_{20}, V_{13}	I_0	I_2	V_1	V_3

Table 4.5: Configurations for Hall mobility measurement with forward magnetic field, $+\vec{B}$.

Configuration	Measurement parameter	I+	I-	V+	V-
13	I_{13}, V_{20}	I_1	I_3	V_2	V_0
14	I_{31}, V_{20}	I_3	I_1	V_2	V_0
15	I_{20}, V_{13}	I_2	I_0	V_1	V_3
16	I_{20}, V_{13}	I_0	I_2	V_1	V_3

Table 4.6: Configurations for Hall mobility measurement with reverse magnetic field, $-\vec{B}$.

Configuration	Measurement parameter	I+	I-	V+	V-
17	I_{13}, V_{20}	I_1	I_3	V_2	V_0
18	I_{31}, V_{20}	I_3	I_1	V_2	V_0
19	I_{20}, V_{13}	I_2	I_0	V_1	V_3
20	I_{20}, V_{13}	I_0	I_2	V_1	V_3

Table 4.7: Type of semiconductor (n-type or p-type) by comparing the voltage.

Configuration	Compare voltage	n-type semiconductor	p-type semiconductor
9,13	$V_{13}-V_9$	+	-
10,14	$V_{14}-V_{10}$	-	+
11,15	$V_{15}-V_{11}$	-	+
12,16	$V_{16}-V_{12}$	+	-
9,17	$V_{17}-V_9$	-	+
10,18	$V_{18}-V_{10}$	+	-
11,19	$V_{19}-V_{11}$	+	-
12,20	$V_{20}-V_{12}$	-	+

4.4.3 Structural Characterization

X-ray diffraction (XRD) analysis was used to investigate the crystallographic properties of the ZnO(Al) films using a Bruker D8 system with Cu-K α radiation ($\lambda=1.5405 \text{ \AA}$). To check all possible peaks of intensity that were detected from the ZnO(Al) thin films, the system was set to perform a rough scan with a step scan of 0.1° and a step time of 0.6 s. The current and voltage of the system were set at 30 mA and 40 kV, respectively. For a fine scan, the system was set to the range of 2θ which

scanned only the peaks in displayed 2θ regions detected from a rough scan. The system was set with a step scan of 0.015° and a step time of 3 s for fine scan. The peak from a fine scan was used to calculate the grain size of films using the *FWHM*. During the measurement, the sample was rotated with a degree of θ while the X-ray detector moved with degree 2θ corresponding with Bragg's law. Table 4.8 shows the typical diffraction angles (2θ) corresponding to the Bragg angles for wurtzite ZnO powder (JCPDS 05-0664).

Table 4.8: Diffraction angles (2θ) of ZnO powder.

2θ	<i>I</i>	<i>h</i>	<i>k</i>	<i>l</i>	2θ	<i>I</i>	<i>h</i>	<i>k</i>	<i>l</i>
31.750	71	1	0	0	95.311	10	2	1	1
34.440	56	0	0	2	98.632	5	1	1	4
36.252	100	1	0	1	102.923	4	2	1	2
47.543	29	1	0	2	104.169	7	1	0	5
56.555	40	1	1	0	107.448	1	2	0	4
62.870	35	1	0	3	110.378	4	3	0	0
66.388	6	2	0	0	116.288	12	2	1	3
67.917	28	1	1	2	121.562	6	3	0	2
69.057	14	2	0	1	125.234	1	0	0	6
72.610	3	0	0	4	133.975	6	2	0	5
76.956	5	2	0	2	136.618	2	1	0	6
81.405	3	1	0	4	138.511	2	2	1	4
89.630	10	2	0	3	142.905	5	2	2	0
92.777	4	2	1	0					

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