Chapter 3

Theoretical Analysis of Thin Film Properties

In this chapter, characterization of electrical, optical and structural properties of thin film will be discussed. The electrical properties were obtained using Hall effect measurement with Van der Pauw technique. The optical properties, such as transmission and absorption coefficient, can be determined from optical transmission measurement. The result from the optical measurement can be used to determine the thickness of the film using the interference from the transmission patterns. The structural properties such as crystal structure and crystallinity are characterized by X-ray diffraction.

3.1 Electrical Properties

The study of carrier transport is important in the development of semiconductor materials. The determination of the simple parameters, such as resistivity, evolves from basic experimental configurations. One of these is the four-point probe method, as shown in Fig. 3.1. The current is injected to the material and the current density ($\overrightarrow{J}$) is written as

$$\overrightarrow{J} = nq\overrightarrow{v}, \tag{3.1}$$

where n is the carrier concentration, q is the electronic charge and $\overrightarrow{v}$ is the drift velocity of the carriers. The relationship between the drift velocity and electric field

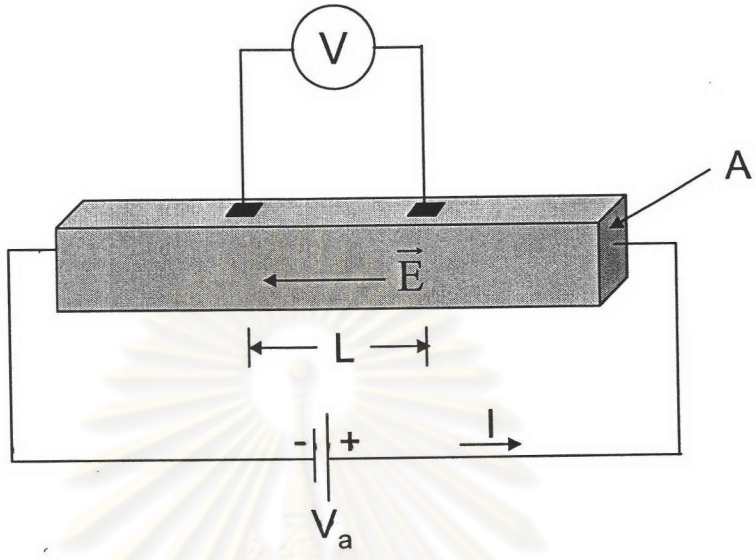

Figure 3.1: Configuration for 4-point probe method for determination of thin film resistivity [23]

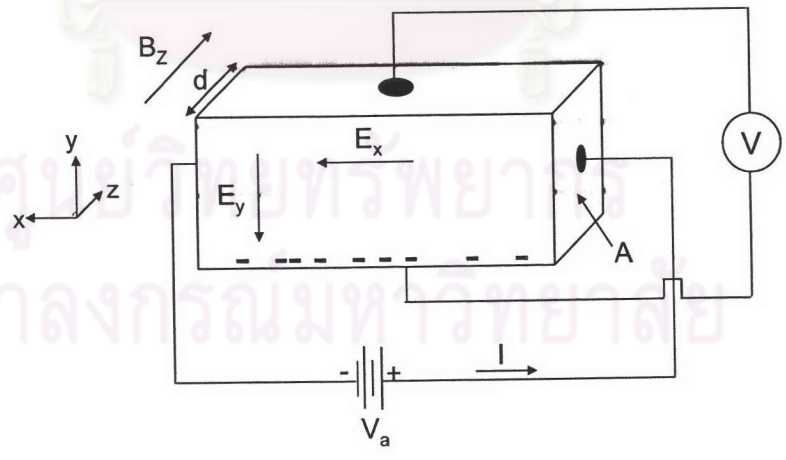

Figure 3.2: Configuration for Hall effect measurement on rectangular-shaped sample that is n-type semiconductor [23]

$(\vec{E})$ is given by

$$\vec{v} = \mu \vec{E}, \tag{3.2}$$

where μ is the mobility of the carriers. Then, Eq. 3.1 can be written as

$$\vec{J} = nq\mu \vec{E}. \tag{3.3}$$

From Ohm's law, the current density is directly proportional to the electric field, and can be written as

$$\vec{J} = \sigma \vec{E}, \tag{3.4}$$

where σ is the conductivity of the material. From Eqs. 3.3 and 3.4, the resistivity (ρ) can be then expressed as

$$\rho = \frac{1}{\sigma} = \frac{1}{nq\mu}. \tag{3.5}$$

The Hall effect and its derivative measurement schemes provide some of the most important information on the majority carrier properties of thin films. The physics of this method is presented in shortened detail, and it is an important background for understanding such technique.

3.1.1 Hall Effect

Consider an experimental configuration for a rectangular shaped sample shown in Fig. 3.2. For an n-type semiconductor, such as the ZnO thin films, the magnetic force $(\vec{F})$, which is defined by

$$\vec{F} = q\vec{v} \times \vec{B}, \tag{3.6}$$

where $\vec{v}$ is the velocity of the carriers and $\vec{B}$ is the applied magnetic field, causes an accumulation of negative charges on the lower surface of the film. For this sample geometry, the magnetic force in the -y direction driving the negative carriers (electron) is

$$F_y = -qv_x B_z. \tag{3.7}$$

If the negative carriers have a mobility (μ_n), then

$$v_x = \mu_n E_x. \tag{3.8}$$

The force is then rewritten as

$$F_y = -q\mu_n E_x B_z. \tag{3.9}$$

The electric field (E_y) in the -y direction is created by the effect of accumulated electrons. This field is a measurable quantity and is called Hall field (E_H), given by

$$E_y = E_H = \frac{V_H}{d}, \tag{3.10}$$

where d is the film thickness and V_H is the Hall voltage that is measured when no current flows in y direction. The force resulting from the Hall field cancels the effect of the magnetic force such that no vertical (y direction) current flows. At equilibrium, $J_y = 0$, then $F_y = 0$ and it can be written as

$$qE_y = q\mu_n E_x B_z. \tag{3.11}$$

As a result, the mobility can be calculated from the measured Hall field,

$$\mu_n = \frac{E_y}{E_x B_z}. \tag{3.12}$$

The measured quantity in this measurement is E_y while the externally controlled parameters are J_x and B_z. The Hall coefficient (R_H) is defined as

$$R_H = \frac{E_y}{J_x B_Z}. \tag{3.13}$$

From Eqs. 3.1, 3.8 and 3.12, one obtains

$$R_H = -\frac{1}{nq}. \tag{3.14}$$

Similar relations can be derived for the analogous p-type semiconductor with appropriate changes in polarities in the equations. In compensated semiconductor samples, where both negative charges (electrons) and positive charges (holes) are present, R_H is given by [23]

$$R_H = \frac{1}{q}\left[\frac{p - nb^2}{(p + nb)^2}\right], \tag{3.15}$$

where n and p are the concentration of negative and positive charges, respectively, and b is the mobility ratio, μ_n/μ_p.

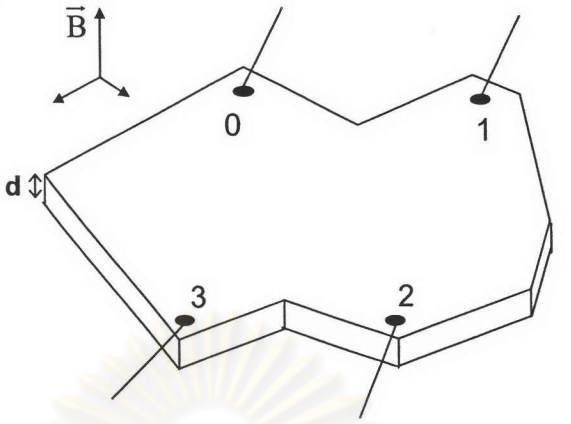

Figure 3.3: Van der Pauw measurement for irregularly-shaped and uniform thickness film

3.1.2 Van der Pauw Technique

One limitation of the Hall effect measurement described in the previous section is the requirement that the sample be in the shape of a rectangular bar. In many cases, real samples are not rectangular slabs of semiconductor materials. This complicates the Hall measurement. Irregularly shaped films with uniform thickness can be analyzed very easily by using the Van der Pauw technique, as illustrated in Fig. 3.3. The electrical contacts at the edge of a sample and their sizes must be much smaller than circumference of a sample which are the important conditions for using this technique.

The current is fed through the contacts 0 and 1 while the voltage is measured at the contacts 2 and 3, then the resistance $R_{01,23}$ is

$$R_{01,23} = \frac{V_{23}}{I_{01}}. \tag{3.16}$$

Similarly, the current is fed through the contacts 1 and 2 while the voltage is measured at the contacts 3 and 0, then the resistance $R_{12,30}$ is

$$R_{12,30} = \frac{V_{30}}{I_{12}}. \tag{3.17}$$

From Eqs. 3.16 and 3.17, the resistivity (ρ) can be calculated by using Van der

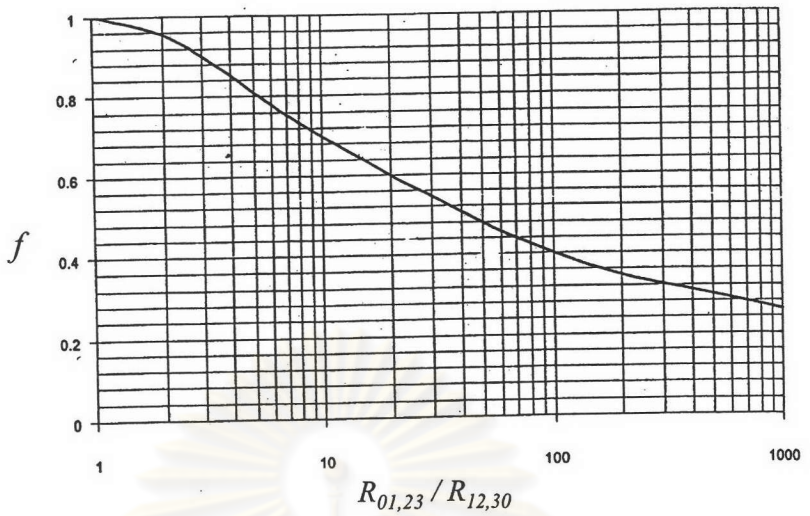

Figure 3.4: Correction factor, f, as a function of resistance ratio [25]

Pauw's Theorem [23] which states that

$$\exp\left(-\frac{\pi R_{01,23}d}{\rho}\right)+\exp\left(-\frac{\pi R_{12,30}d}{\rho}\right)=1. \tag{3.18}$$

This relationship applies to any arbitrary-shaped sample. The resistivity can be defined in terms of two sets of measurement of transverse resistivity. After some algebraic manipulation, one obtains

$$\rho=\frac{\pi d}{\ln 2}\left[\frac{R_{01,23}+R_{12,30}}{2}\right]f\left(\frac{R_{01,23}}{R_{12,30}}\right), \tag{3.19}$$

where f is the correction function depending on the ratio $R_{01,23}/R_{12,30}$, as shown in Fig. 3.4. For symmetrically placed contacts, f is equal to 1 and the resistance ratio is exactly 1. In the mobility measurement, Van der Pauw technique is used under the magnetic field. The current is input from the contact 0 to 2 while the voltage is measured across the contacts 1 and 3. The voltage is usually measured both with forward magnetic field $(+\vec{B})$ and reverse magnetic field $(-\vec{B})$. Van der Pauw showed that the Hall coefficient is given by [27]

$$R_H=\frac{d}{2B}\Delta R_{02,13}, \tag{3.20}$$

where the value $\Delta R_{02,13}$ specifies the change in resistance with the forward and reverse magnetic field. Therefore, the Hall mobility can be calculated from

$$\mu=\frac{R_H}{\rho}=\frac{d}{2B\rho}\Delta R_{02,13}. \tag{3.21}$$

Then, the carrier concentration can be determined from Eq. 3.5 with the expression

$$n = \frac{1}{q\rho\mu}. \tag{3.22}$$

3.2 Optical Properties

3.2.1 Optical Technique for Measuring Film Thickness

The optical measurement method is one of easy, quick and nondestructive techniques used to determine the thickness of transparent thin films with generally high accuracy. The key basic principle is based on the interference of two beams of light whose optical path difference is related to the film thickness [23, 28]. The incoming beam is incident on a thin film that is grown on a transparent substrate such as a soda-lime glass (SLG).

For better understanding, the beam of light which produces the interference in thin film can be shown in Fig. 3.5. The simplest ideal case is a film surface and substrate that are perfectly flat and has a uniform thickness. The transmission (T) of the system depends on the parameters such as the optical constants, the film thickness, the wavelength of the light and the indices of refraction (n) of the substrate and the medium above the film. The films thickness can be calculated from interference patterns or fringes of the optical transmission of thin films.

In Fig. 3.5, consider a GZO thin film of uniform thickness d and index of refraction n_{GZO}. The light beams travelling in air are nearly normal to the surface of the film. For the change of phase due to reflection, a wave traveling from a medium of refractive index n_1 toward a medium of refractive index n_2 undergoes a 180° phase change upon reflection when $n_2 > n_1$ and no phase change if $n_2 < n_1$. The wavelength of light λ_n in a medium whose refractive index n is

$$\lambda_n = \frac{\lambda}{n}, \tag{3.23}$$

where λ is the wavelength of the light in free space. From Fig. 3.5, the beam 1 thus undergoes no phase change with respect to the incident beam because it

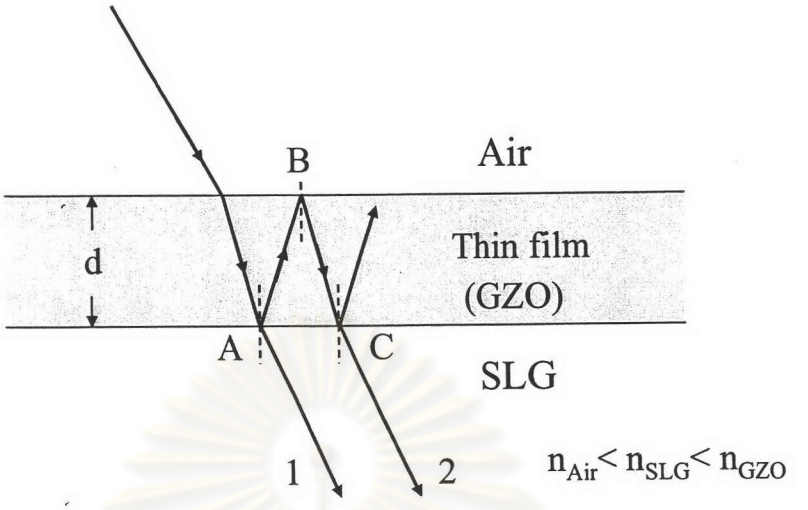

Figure 3.5: Interference in light beam transmitted from a thin film is due to a combination of beams 1 and beam 2

is a transmitted beam at the point A. Since $n_{SLG} < n_{GZO}$, the reflected beam at the point A, which is reflected from the lower film surface, undergoes no phase change. The beam 2, which is reflected from the upper surface at the point B and then transmitted through the film at the point C, also undergoes no phase change because of $n_{Air} < n_{GZO}$ at the point B. Therefore, the beam 1 has the same phase with the beam 2.

However, the beam 2 travels a distance $2d$ before the beam transmits at the point C. The waves recombine in phase when they transmit through the film and transparent substrate. The result is the interference of transmitted beams of light.

Two distinct wavelength regions generally occur for semiconductor. At long wavelengths (photon energies less than the bandgap), the transmission (T) exhibits oscillations from interference effects in the transparent film. At short wavelength (photon energies greater than the bandgap), T rapidly decreases to zero. Such a typical relationship between transmission and wavelength is presented in Fig. 3.6.

The notation T_{Max} and T_{Min} refer to the value of the maximum and minimum in T, respectively. In general, the condition for constructive interference (T_{Max}) in

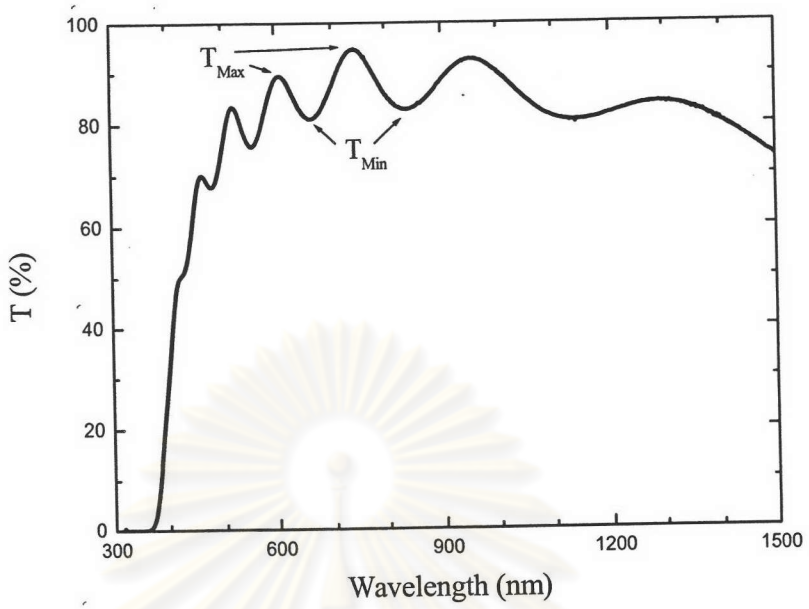

Figure 3.6: Optical transmission spectrum of the GZO film as a function of wavelength and the result shows the oscillations due to interference in thin film

such situation is

$$2d = m\lambda_n, \tag{3.24}$$

where m = 0, 1, 2, ..., and destructive interference (T_{Min}) satisfy the same quality with m = $\frac{1}{2}, \frac{3}{2}, \ldots$ in the long wavelength region. From Eq. 3.23, then Eq. 3.24 can be written as

$$2nd = m\lambda. \tag{3.25}$$

Consider two maxima or two minima of the transmission patterns according to wavelengths λ_1 and λ_2, the number of oscillations (M) between the two extreama is

$$M = m_1 - m_2. \tag{3.26}$$

From Eq. 3.25, we can write

$$M = 2nd\left|\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right| = \frac{2nd}{\lambda_1\lambda_2}\left|\lambda_2 - \lambda_1\right|. \tag{3.27}$$

Therefore, the film thickness (d) can be determined according to

$$d = \frac{M\lambda_1\lambda_2}{2n\left|\lambda_2 - \lambda_1\right|}. \tag{3.28}$$

3.2.2 Optical Absorption Properties

Radiation absorption occurs in the majority of media. The intensity I of a light wave in the thin film decreases as [23]

$$I = I_0 \exp(-\alpha x), \tag{3.29}$$

where x is the distance into the film from surface under illumination. The quantity α is the absorption coefficient and is related to the imaginary part k of the refractive index through the expression [23]

$$\alpha = \frac{4\pi k}{\lambda}, \tag{3.30}$$

where λ is the wavelength of light in vacuum. Absorption is a phenomenon of fundamental interest because of its relation to the dynamics of the electrons and ions of the film under the influence of electromagnetic radiation. The electrons absorb energy of radiation that is equal to or higher than bandgap of semiconductors for interband (band-to-band) transition from the maximum point of valence band to the minimum point of conduction band. Therefore, the absorption edge is defined by the minimum energy of radiation for interband transitions of the electrons. The interband transition can be divided into the following:

Allowed direct transitions, [29]

$$\alpha = \frac{A}{h\nu}(h\nu - E_g)^{\frac{1}{2}}. \tag{3.31}$$

Forbidden direct transitions, [29]

$$\alpha = \frac{B}{h\nu}(h\nu - E_g)^{\frac{3}{2}}. \tag{3.32}$$

Indirect transitions [29],

$$\alpha = \frac{C}{h\nu}(h\nu - E_g)^2. \tag{3.33}$$

where A, B, C are the constants, $h\nu$ is the photon energy and E_g is the energy gap of the semiconductor. For the ZnO thin films, which is the direct bandgap

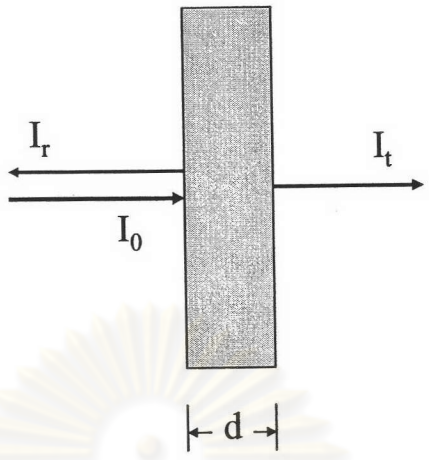

Figure 3.7: Transmission and Reflection of the film

semiconductor, the interband transition is the allowed direct transition because the electrons transit from valence band to conduction band at the same wave vector. Then, the simple parabolic band can be used for interband transition model of ZnO thin films.

3.2.3 Determination for Absorption Coefficient

Concider a normal incidence, as shown in Fig. 3.7, the absorption coefficient can be calculated directly from the transmission of the films. The transmission (T) and the reflection (R) can be expressed in terms of the intensity of incident wave I_0, intensity of transmitted wave I_t and intensity of reflected wave I_r as the followings [29];

$$T = \frac{I_t}{I_0} = \frac{(1-R)^2 \exp(-\alpha d)}{1 + R^2 \exp(-2\alpha d)}, \tag{3.34}$$

$$R = \frac{I_r}{I_0} = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \tag{3.35}$$

If the film has a large thickness (d), then $R^2 \exp(-2\alpha d) << 1$ and Eq. 3.34 can be reduced to

$$T = (1-R)^2 \exp(-\alpha d). \tag{3.36}$$

In general, the changing of photon energy of incident wave affects the reflection (R) slightly. Then, the term $(1-R)^2$ can be approximated to a constant. From Eq. 3.36, the optical absorption coefficient is

$$\alpha = \frac{1}{d}\ln(\frac{I_0}{I_t}) + C, \tag{3.37}$$

where C is a constant. Since the reflection is approximated by a constant, the absorption coefficient is higher than a real value. In experiments, the background absorption coefficient (α_0) caused by the imperfection of thin film is subtracted for the correct absorption coefficient determination.

3.3 Structural Properties

The crystal structure of the films can be determined from an X-ray diffraction (XRD) pattern. The important theory that involves this phenomenon will be described in this section.

3.3.1 X-ray Diffraction (XRD)

X-ray is the electromagnetic wave that has high transmission through the medium. The wavelength, which is suitable for measuring the crystal structure, is in the range from 0.5Å to 3Å that is shorter than the interplanar spacing (d) of the crystal for the diffraction to occur. The crystal can be seen that it is composed of the arranged parallel planes of atoms. Then, the incident beams of X-ray are reflected from these planes in the crystal, with each plane reflecting only a small fraction of the radiation. The angle of incidence is equal to the angle of reflection. The diffracted beams are found when the reflections from parallel planes interfere constructively and destructively, as shown in Fig. 3.8. The path difference for X-ray reflected from adjacent planes is $2d\sin\theta$, where θ called Bragg angle is measured from plane. Constructive interference of the radiation occurs when the path difference is an integer number n of wavelengths (λ) of X-ray, so that

$$2d\sin\theta = n\lambda. \tag{3.38}$$

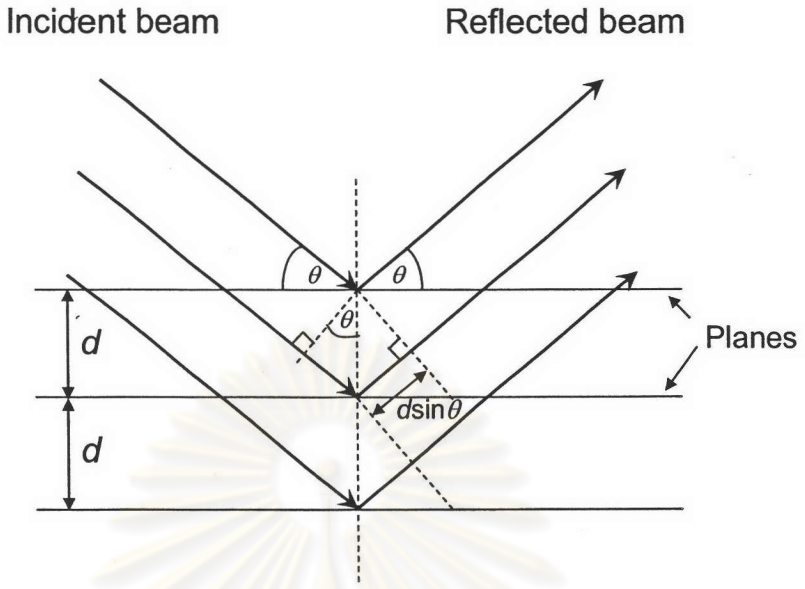

Figure 3.8: Diffraction of X-ray from parallel planes in the crystal followed by Bragg law

Equation 3.38 is known as the Bragg law [30]. The interference patterns can be observed by measuring intensities of diffracted X-ray at varied diffraction angles (2θ), which are the angles between reflected beams and incident beams. For the same element or material, there is the highest intensity of constructively interference at the same diffraction angle. The interplanar spacing of (hkl) plane can be defined that $d = d_{hkl}$, where h, k and l are Miller indicies. The planes in the crystal are indicated by miller indicies. The relationship between the Miller indicies, lattice constants (a, b, c) and interplanar spacing for ZnO of which crystal structure is wurtzite structure composed of two hexagonal closed-packs ($a = b$) can be expressed as [2, 3]

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}. \tag{3.39}$$

Therefore, the lattice constants of ZnO can be calculated from Eq. 3.39. For ZnO powder standard (JCPDS 05-0664), the lattice constants $a = 3.249$Å and $c = 5.205$Å.