

## CHAPTER 3

### ANALYTICAL METHODS OF THIN FILMS

Theoretical backgrounds involved in the analysis of the films will be described in this chapter. The deposited films are analyzed for their electrical, optical and structural properties. The electrical properties such as electrical resistivity, Hall mobility and carrier concentration are obtained from Hall effect measurement using the Van der Pauw method. 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 energy gap and the thickness of the film using the interference from the transmission spectrum. The structural properties in terms of crystallinity and crystallite size of thin films are characterized by X-ray diffraction method.

#### 3.1 Electrical Properties

##### 3.1.1 Resistivity

Consider a semiconductor sample shown in Fig. 3.1, which has a cross-sectional area  $A$ , a length  $L$ , and a carrier concentration of  $n$  electrons /  $\text{cm}^3$ . Suppose we apply an electric field  $\vec{E}$  to the sample.

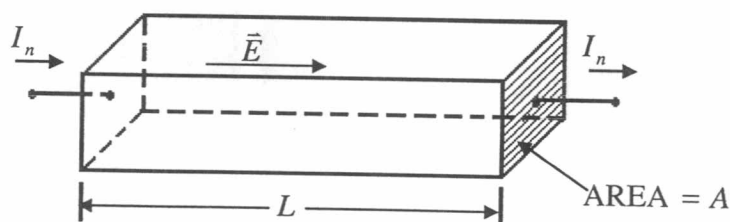


Figure 3.1: Current conduction in a uniformly doped semiconductor bar with length  $L$ , and cross-sectional area  $A$ .

The electron current density  $\vec{J}_n$  flowing in sample is

$$\vec{J}_n = \frac{I_n}{A} = -qn\vec{v}_n, \quad (3.1)$$

where  $I_n$  is the electronic current,  $q$  is the electronic charge and  $\vec{v}_n$  is the drift velocity of the electron. The relationship between the drift velocity and the electric field is given by

$$\vec{v}_n = -\mu_n\vec{E}, \quad (3.2)$$

where  $\mu_n$  is the electron mobility in the unit of  $\text{cm}^2 / \text{V}\cdot\text{s}$ . Thus the Eq. 3.1 can be written as

$$\vec{J}_n = qn\mu_n\vec{E}. \quad (3.3)$$

A similar argument is also applied when we consider holes as carriers instead of electron. By taking the charge on the hole to be positive, we have

$$\vec{J}_p = qp\vec{v}_p = qp\mu_p\vec{E}. \quad (3.4)$$

The total current flowing in the semiconductor sample due to the applied electric field  $\vec{E}$  can be written as the sum of the electron and hole current component:

$$\vec{J} = \vec{J}_n + \vec{J}_p = (qn\mu_n + qp\mu_p)\vec{E}. \quad (3.5)$$

The quantity in parentheses is known as *conductivity*:

$$\sigma = (qn\mu_n + qp\mu_p). \quad (3.6)$$

The resistivity of the semiconductor, which is the inverse of  $\sigma$ , is given by

$$\rho \equiv \frac{1}{\sigma} = \frac{1}{q(n\mu_n + p\mu_p)}. \quad (3.7)$$

Generally, in extrinsic semiconductors, only one of the components in Eq. 3.5 or 3.6 is significant due to the many order of magnitude difference between the two carrier densities. Therefore, Eq. 3.7 reduces to

$$\rho = \frac{1}{qn\mu_n} \quad (3.8)$$

for an n-type semiconductor and to

$$\rho = \frac{1}{qp\mu_p} \quad (3.9)$$

for a p-type semiconductor.

### 3.1.2 The Van der Pauw Method

The most common method for measuring resistivity is the Van der Pauw method which is the four-point probe technique. This technique can be used to analyze arbitrary shaped sample without knowing the current pattern, as illustrated in Fig 3.2.



Figure 3.2: A flat arbitrary shaped sample with four small contacts 0, 1, 2 and 3 on the periphery.

The resistivity can be correctly measured, if the following conditions are met [28]: (1) the contacts are at the circumference of the sample, (2) the contacts are sufficiently small, (3) the sample has a uniform thickness and (4) the surface of the sample is singly connected, i.e. the sample does not contain any isolated holes.

Consider a semiconductor sample of arbitrary shape with four small electrical contacts: 0, 1, 2 and 3 at arbitrary places on the periphery satisfying the conditions above as shown in Fig. 3.2. The small current  $I_{01}$  from a constant current source is fed through the contact 0 and taken out at the contact 1 and the voltage is measured between the contacts 2 and 3. The resistance

$$R_{01,23} = \frac{V_{23}}{I_{01}}. \quad (3.10)$$

Similarly, the current  $I_{12}$  is fed through the contact 1 and taken out at the contact 2 while the voltage is measured between the contacts 3 and 0. The resistance  $R_{12,30}$  is

$$R_{12,30} = \frac{V_{30}}{I_{12}}. \quad (3.11)$$

From Eqs.3.10 and 3.11, between  $R_{01,23}$  and  $R_{12,30}$  there exists a simple relation [28]

$$\exp\left(\frac{-\pi d R_{01,23}}{\rho}\right) + \exp\left(\frac{-\pi d R_{12,30}}{\rho}\right) = 1, \quad (3.12)$$

where  $d$  is the thickness of the sample and  $\rho$  is the resistivity of the material. If  $d$  and the resistance  $R_{01,23}$  and  $R_{12,30}$  are known, the resistivity can be calculated from

$$\rho = \frac{\pi d}{\ln 2} \left[ \frac{R_{01,23} + R_{12,30}}{2} \right] f \left( \frac{R_{01,23}}{R_{12,30}} \right), \quad (3.13)$$

where  $f$  is the correction factor depending on the ratio  $\frac{R_{01,23}}{R_{12,30}}$  as shown in Fig. 3.3.



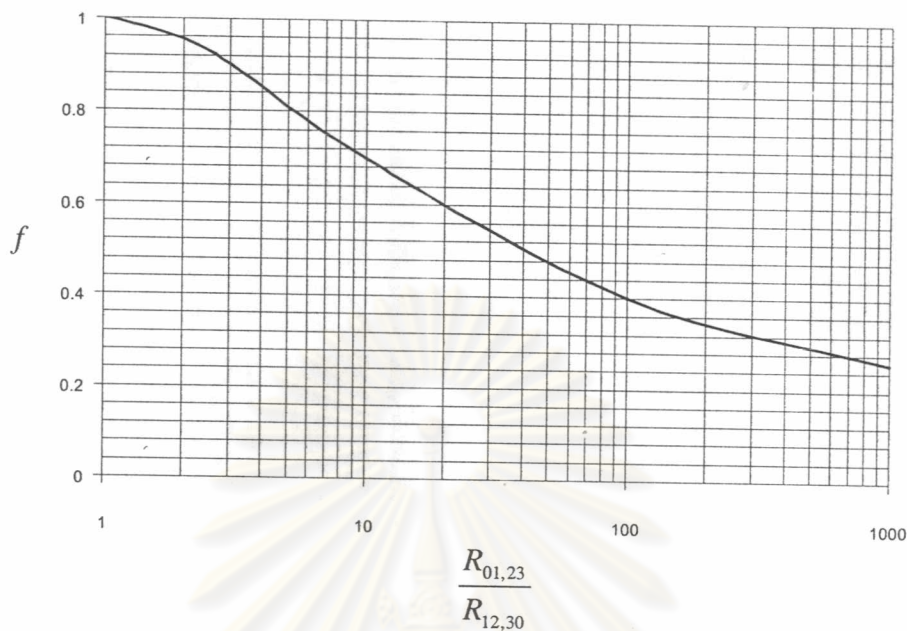


Figure 3.3: Correction factor,  $f$  as a function of resistance ratio [17].

Thus, to determine  $\rho$ , we first calculate  $\frac{R_{01,23}}{R_{12,30}}$ , read the correction factor  $f$  from Fig. 3.3 and then find  $\rho$  from the Eq. 3.13.

In particular case, if the sample possesses a line of symmetry then in this case the contacts 0 and 2 are placed on the line of symmetry, while the contacts 1 and 3 are disposed symmetrically with respect to this line (Fig. 3.4). Then

$$R_{01,23} = R_{12,30} \quad (3.14)$$

and the ratio  $\frac{R_{01,23}}{R_{12,30}}$  is equal to 1, so the value of  $f$  from Fig. 3.3 is equal to 1. The

resistivity can easily be found from Eq. 3.13;

$$\rho = \frac{\pi d}{\ln 2} R_{01,23} \quad (3.15)$$

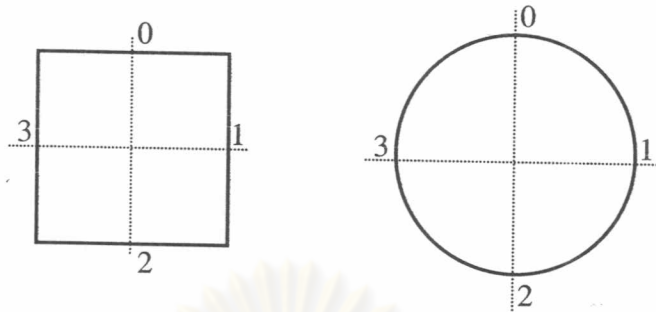


Figure 3.4: The samples with four small contacts 0, 1, 2 and 3 on the symmetry lines.

### 3.1.3 The Hall Effect Measurement

The Hall effect measurement is the most commonly used method to determine the carrier type and concentration in the semiconductor sample.

Consider an n-type semiconductor sample, as shown in Fig. 3.5, with an applied electric field along the  $-x$  direction and an applied magnetic field along the  $z$  direction.

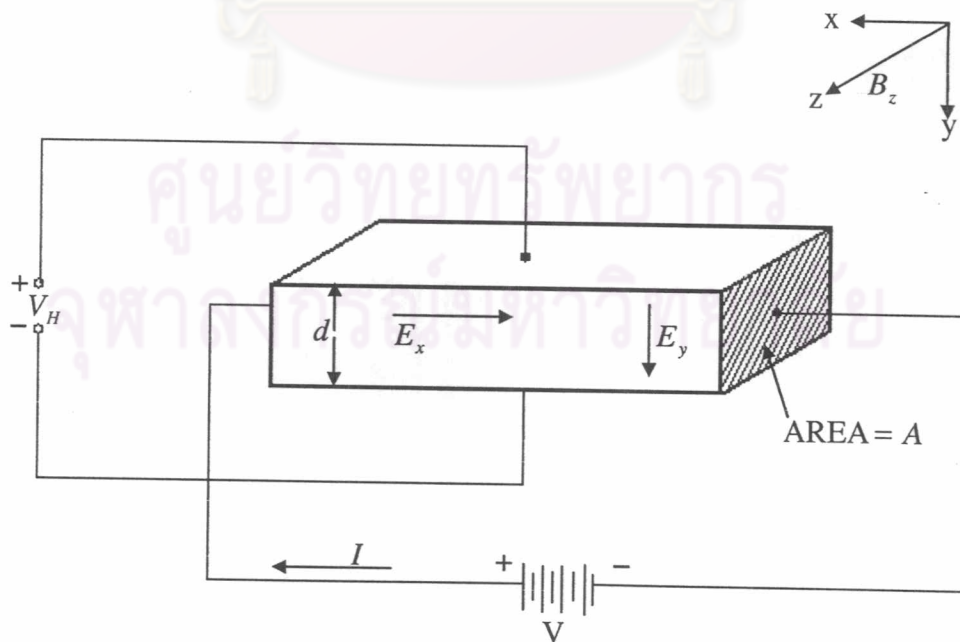


Figure 3.5: Basic setup to measure carrier concentration using the Hall effect.

The Lorentz force,  $q\vec{v} \times \vec{B} (= -qv_x B_z)$  due to the magnetic field will exert an average downward force on the electrons flowing in the x direction. The downward-directed current causes an accumulation of electrons at the bottom of sample giving rise to a downward-directed electric field  $E_y$ . The establishment of the electric field  $E_y$  is known as the *Hall effect*. In the steady state, there is no net current flowing along the y direction, the force due to the electric field along the y direction will cancel out the magnetic force, that is

$$qE_y = qv_x B_z \quad (3.16)$$

or

$$E_y = v_x B_z. \quad (3.17)$$

The electric field in Eq. 3.17 is called the *Hall field* and the *Hall voltage* is given by  $V_H = E_y d$ . Using Eq. 3.1 for the electron drift velocity, the Hall field  $E_y$  in Eq. 3.17 becomes

$$E_y = -\left[\frac{J_n}{qn}\right] B_z = R_H J_n B_z, \quad (3.18)$$

where

$$R_H \equiv -\frac{1}{qn}. \quad (3.19)$$

The Hall field  $E_y$  is proportional to the product of the current density and the magnetic field. The proportionality constant  $R_H$  is the *Hall coefficient*. A similar result can be obtained for a p-type semiconductor, except the Hall coefficient is positive:

$$R_H = \frac{1}{qp}, \quad (3.20)$$

where  $p$  is the carrier concentration of holes. For the case of mixed conduction (i.e. an appreciable number of both holes and electrons), the Hall coefficient has a contribution from each carrier. Then  $R_H$  is given by [29]

$$R_H = \frac{(1/q)(p - b^2n)}{(bn + p)^2}, \quad (3.21)$$

where  $b$  is the ratio of electron-to-hole conduction mobility ( $b = \mu_n/\mu_p$ ).

The measurement of the Hall voltage for a known current and magnetic field yields

$$n = -\frac{1}{qR_H} = -\frac{J_n B_z}{qE_y} = -\frac{(I/A)B_z}{q(V_H/d)} = -\frac{IB_z d}{qV_H A}, \quad (3.22)$$

where all the quantities on the right-hand side of the equation can be measured. Thus, the carrier concentration can be obtained directly from Eq. 3.22. Similar result can be obtained for hole,

$$p = \frac{1}{qR_H} = \frac{J_p B_z}{qE_y} = \frac{(I/A)B_z}{q(V_H/d)} = \frac{IB_z d}{qV_H A}. \quad (3.23)$$

### 3.1.4 Hall Mobility

The *Hall mobility* is defined by [29]

$$\mu = \frac{|R_H|}{\rho} = |R_H| \sigma. \quad (3.24)$$

Since  $\rho$  is shape-independent as discussed in section 3.1.1, the Hall mobility can then be measured on an arbitrary shaped sample, using the Van der Pauw technique under the magnetic field. The current was applied to one of the contacts, such as contact 0, and taken off at the contact 2. The voltage is then measured between the contacts 1 and 3. The resistance  $R_{02,13}$  is obtained by



$$R_{02,13} = \frac{V_{13}}{I_{02}}. \quad (3.25)$$

We measured  $R_{02,13}$  both with applied magnetic field and without applied magnetic field. This changes  $R_{02,13}$  by an amount  $\Delta R_{02,13}$ . Then the Hall coefficient is given by

$$R_H = \frac{d}{B} \Delta R_{02,13}, \quad (3.26)$$

and the Hall mobility can be calculated from

$$\mu = \frac{R_H}{\rho} = \frac{d}{B\rho} \Delta R_{02,13}. \quad (3.27)$$

## 3.2 Optical Analysis

### 3.2.1 Optical Method for Measuring Film Thickness

The measurement of the thickness of transparent thin films using transmitted light is a well-established technique [30]. Such optical technique for the determination of thin film characteristics involves the interaction of the film with electromagnetic radiation. It can be said that this technique is easy, nondestructive and high accuracy for measurement. In addition, the optical technique can be used to determine the optical constants such as the refractive index and absorption coefficient.

A schematic diagram of the transmitted light through a transparent thin film such as ZnO(Al) thin film is shown in Fig 3.6. The ZnO(Al) film was deposited on a transparent substrate such as a soda-lime glass (SLG).

Consider the ZnO(Al) film of a uniform thickness  $d$  and an index of refraction  $n_{\text{ZnO(Al)}}$ . Assume that the light rays traveling in air are nearly normal to the surface of the film. It is a fundamental property of optics that the light pass through an interface between materials of different indices of refraction will be divided into transmitted and reflected components. To determine whether the reflected or transmitted rays interfere constructively or destructively, we first note the following facts:

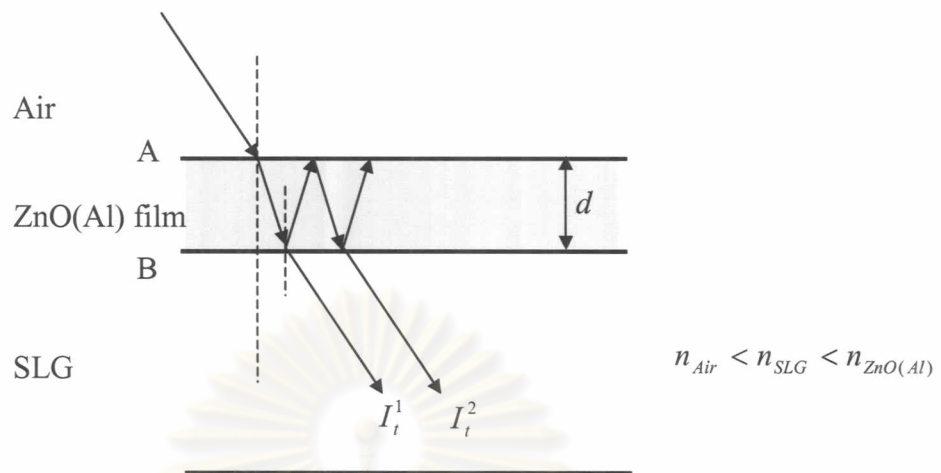


Figure 3.6: Interference caused by light traveling different paths through a film.

- A wave traveling from a medium of index of refraction  $n_1$  toward a medium of index of refraction  $n_2$  undergoes a  $180^\circ$  phase change upon reflection when  $n_2 > n_1$  and undergoes no phase change if  $n_2 < n_1$ .
- The wavelength of light  $\lambda_n$  in a medium whose refraction index is  $n$  is

$$\lambda_n = \frac{\lambda}{n}, \quad (3.28)$$

where  $\lambda$  is the wavelength of the light in free space.

Let us apply these rules to the film in Fig 3.6, where  $n_{\text{ZnO(Al)}} > n_{\text{Air}}$ . The transmitted ray 1,  $I_t^1$ , which is transmitted from the lower film surface (B) undergoes no phase change with respect to the incident wave. The transmitted ray 2,  $I_t^2$ , which is reflected from the upper film surface (A) undergoes no phase change because it is reflected from a medium (air) that has a lower index of refraction. Therefore,  $I_t^1$  is in phase with  $I_t^2$ . However,  $I_t^2$  travels an extra distance  $2d$  before the waves recombine under the surface B. If  $2d$  equals to integral number of wavelength, then they recombine in phase and the result is a constructive interference. In general, the

condition for light transmitted through a film, a maximum in intensity,  $T_{Max}$  will occur when

$$2d = m\lambda_n, \quad (3.29)$$

where  $d$  is the film thickness and  $m$  is a non negative integer ( $m=0, 1, 2, \dots$ ). Because  $\lambda_n = \lambda/n$ , so we can write Eq. 3.29 as

$$2nd = m\lambda. \quad (3.30)$$

If the extra distance  $2d$  traveled by  $I_t^2$  corresponds to a half-integral multiple of the wavelength  $\lambda_n$ , then the two waves combine out of phase and the result is destructive interference (minimum intensity). The general equation for destructive interference,  $T_{Min}$  is

$$2nd = \left(m + \frac{1}{2}\right)\lambda. \quad (3.31)$$

Equation 3.30 can be used to determine the film thickness through the relationship

$$d = \frac{m\lambda_0}{2n} = \frac{(m+1)\lambda_1}{2n} = \frac{(m+i)\lambda_i}{2n}, \quad (3.32)$$

or  $m = i\lambda_i/[\lambda_0 - \lambda_i]$ , where  $i$  is the number of complete cycles from  $\lambda_0$  to  $\lambda_i$ . For one cycle  $i = 1$ , and

$$d = \frac{1}{2n(1/\lambda_1 - 1/\lambda_0)} = \frac{1}{2n\Delta(1/\lambda)}, \quad (3.33)$$

where  $1/\lambda$  is the wave number and  $\Delta(1/\lambda)$  is the wave number interval between two maxima or minima of the oscillatory transmission curve as indicated in Fig. 3.7.

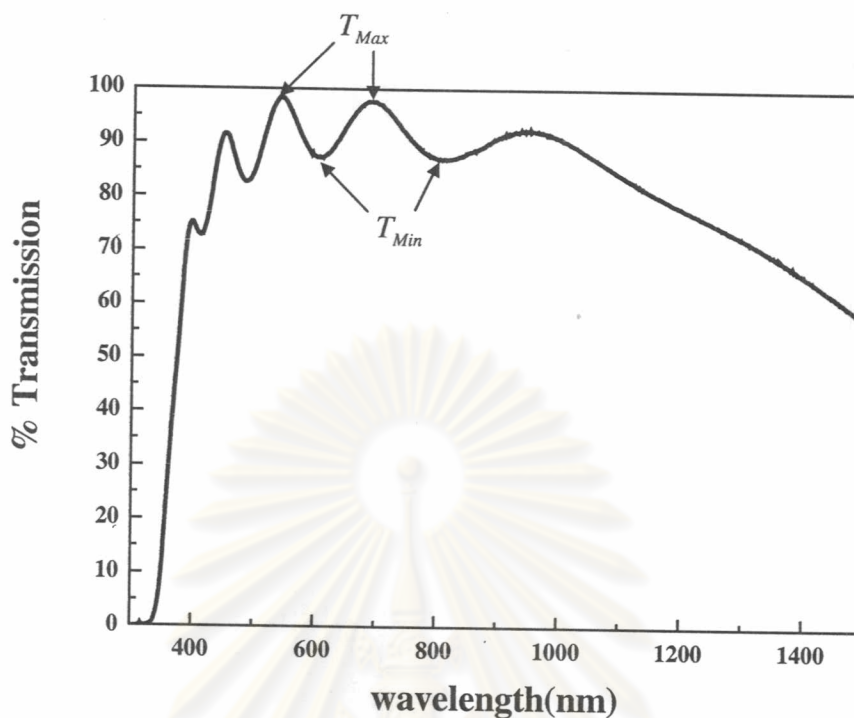


Figure 3.7: Two maxima or minima of the oscillatory transmission curve.

### 3.2.2 Optical Absorption [31]

In Fig. 3.8, we describe basic transitions in a semiconductor. When the semiconductor is illuminated, photons are absorbed to create electron-hole pairs. In the case (a), the photon energy  $h\nu$  is greater than  $E_g$ , an electron-hole pair is generated and the excess energy,  $(h\nu - E_g)$ , is dissipated as heat, while there is no heat dissipation in (b). Both processes are called *intrinsic transitions* or *band-to-band transition*. On the other hand, for  $h\nu$  less than  $E_g$ , a photon will be absorbed only if there are available energy states in the forbidden gap due to the physical defects as shown in Fig. 3.8 (c), and is called *extrinsic transition*. For reverse situation, an electron at the conduction band edge recombines with a hole at the valence band edge resulting in the emission of a photon with energy equal to that of the energy difference.



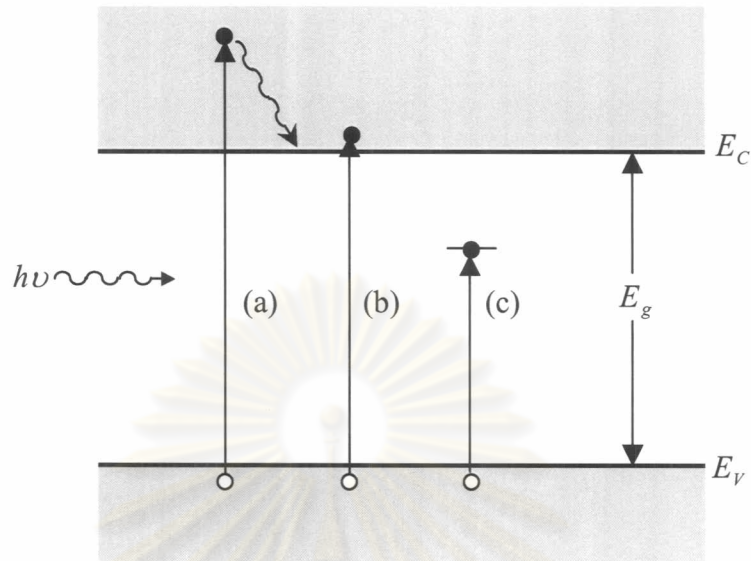


Figure 3.8: Optical absorption for (a)  $h\nu > E_g$ , (b)  $h\nu = E_g$  and (c)  $h\nu < E_g$ .

Now, let us assume that a semiconductor is illuminated by a light source with intensity  $I_0$ . As the light travels through the semiconductor, the transmitted light  $I_t$  is decreased due to the absorption process in the sample. Typically, the absorption is expressed in terms of an *absorption coefficient*,  $\alpha$  which is defined as the relative rate of decrease in light intensity along its propagation path:

$$\alpha = -\frac{1}{I(x)} \frac{dI(x)}{dx}. \quad (3.34)$$

The negative sign indicates decreasing intensity of light due to the absorption. The solution of Eq. 3.34 with the boundary condition  $I(x) = I_0$  at  $x = 0$  is

$$I(x) = I_0 e^{-\alpha x}. \quad (3.35)$$

The intensity that exits from the other side of the semiconductor at  $x = d$  (Fig. 3.9) is

$$I(d) = I_0 e^{-\alpha d}, \quad (3.36)$$

where  $\alpha$  is related to the extinction coefficient  $k$  by

$$\alpha = \frac{4\pi k}{\lambda}, \quad (3.37)$$

where  $\lambda$  is the wavelength of the light in vacuum.

The fundamental absorption refers to band-to-band (intrinsic) transition, which manifests itself by a rapid rise in absorption, can be used to determine the energy gap,  $E_g$ , of the semiconductor. The band-to-band transition can be divided into the following:

Allowed direct transitions, [32]

$$\alpha h\nu = A'(h\nu - E_g)^{1/2}, \quad (3.38)$$

where  $A'$  is constant,  $h\nu$  and  $E_g$  being expressed in eV.

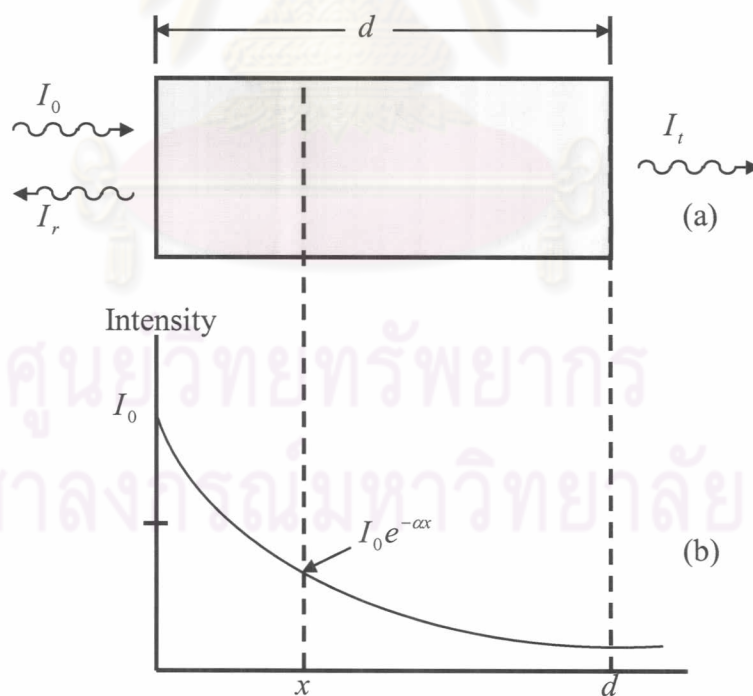


Figure 3.9: Optical absorption: (a) Semiconductor under illumination, (b) Exponential decay of light intensity.

Forbidden direct transition, [32]

$$\alpha h\nu = A^* (h\nu - E_g)^{3/2}, \quad (3.39)$$

where  $A^*$  is constant.

For the ZnO(Al) film, the band-to-band transition is the allowed direct transition. The electrons are excited from the valence band to the conduction band at the same wave vector. Then, the parabolic bands can be used for transition model of ZnO(Al) thin film.

### 3.2.3 Transmission

Consider a normal incidence, as shown in Fig. 3.9 (a), the transmission  $T$  and the reflection  $R$  can be expressed in terms of the intensity of incident light  $I_0$ , the intensity of transmitted light  $I_t$  and the intensity of reflected light  $I_r$ , as the followings [29];

$$T = \frac{I_t}{I_0} = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}}, \quad (3.40)$$

$$R = \frac{I_r}{I_0} = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \quad (3.41)$$

Semiconductors are generally transparent for photon energies less than the energy gap and the product  $\alpha d$  is large, one can neglect the second term in the denominator, then

$$T \approx (1-R)^2 e^{-\alpha d}. \quad (3.42)$$

If  $R$  and  $d$  are known,  $\alpha$  can be obtained from Eq. 3.42. If  $R$  is not known, one can measure the transmission of two samples having different thickness  $d_1$  and  $d_2$ . Then  $\alpha$  is obtained from

$$\frac{T_1}{T_2} \approx e^{\alpha(d_2-d_1)}. \quad (3.43)$$

Note that since  $T_1 = I_{i1}/I_0$  and  $T_2 = I_{i2}/I_0$ , then it is not necessary to know  $I_0$  in using Eq. 3.43 because one can replace  $T_1/T_2$  by  $I_{i1}/I_{i2}$ .

### 3.3 Structural Analysis

X-ray diffraction (XRD) is a technique for determining the crystal structure. The brief theory that involves this phenomenon will be described in this section.

#### 3.3.1 X-Ray Diffraction (XRD)

X-ray is the electromagnetic radiation having the wavelength in the range from  $0.5 \text{ \AA}$  to  $2.5 \text{ \AA}$ . It is suitable for measuring the crystal structure using the diffraction effect.

In Fig. 3.10, the incident beams 1 and 2 of X-ray are reflected from the crystal plane in the crystal. The angle of incidence is equal to the angle of reflection. The diffracted beams 1' and 2' are found when the reflections from parallel planes interfere constructively as shown in Fig. 3.10.

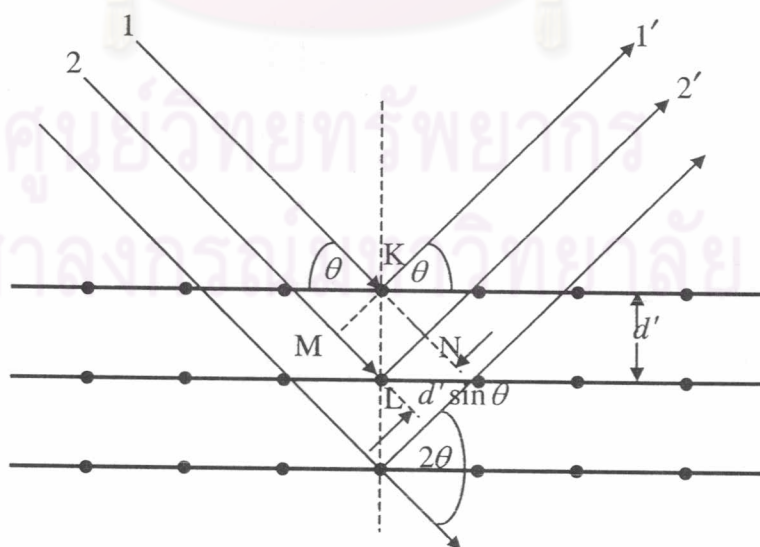


Figure 3.10: Diffraction of X-rays by crystals.



The path different for X-ray reflected from adjacent planes is  $2d' \sin \theta$ . The constructive interference of the radiation occurs when the path difference is an integral number  $n$  of wavelength ( $\lambda$ ) of X-ray, so that

$$2d' \sin \theta = n\lambda. \quad (3.44)$$

This relation was first formulated by W. L. Bragg and known as the *Bragg law*.

### 3.3.2 Crystallite Size

The intensities of diffracted X-rays peaks at varied diffraction angles ( $2\theta$ ), can be used to calculate the crystallite size of sample. The crystallite size or grain size can be estimated using the Scherrer formula [33]:

$$g = \frac{0.9\lambda}{FWHM \cos \theta}, \quad (3.45)$$

where  $g$  is the grain size,  $\lambda$  is the X-ray wavelength,  $\theta$  is the Bragg diffraction angle in degree and  $FWHM$  is the full width at half maximum in radian of the diffracted X-ray peak.

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