Chapter 2
Theoretical Aspects

This chapter gives an account of the fundamental theories of the experimental tools and their implementation, for the characterization of the materials under investigation in the present work. This includes a detailed description of the photo induced changes that occur during the photon–matter interaction which forms the basis of the Photoacoustic (PA) Technique, Density Functional Theory (DFT) to analyse the photo acoustic spectra, determination of electrical properties from ac and dc conductivity measurements and the fundamentals of X-ray Diffraction (XRD), Transmission Electron Microscopic (TEM) and Scanning Electron Microscopic (SEM) investigations.

2.1 Introduction

In the present work, photoacoustic technique has been used as a tool for spectroscopic measurements on the samples, which gives insight into the electronic band structure and its modifications with varying sample compositions and also the thermal transport properties. Spectroscopy is the measurement and interpretation of electromagnetic
(EM) radiation absorbed or emitted when the molecules, atoms or ions of a sample move from one state to another. The laser based spectroscopic techniques can be divided into

a. Absorption measurement method

b. Radiative transition technique

c. Non radiative transition technique

The absorption method is the basic and the simplest approach and by using this technique, information regarding the optical properties and composition of the sample can be obtained by varying different parameters such as intensity, wave length, etc. of the light beam that passes through or gets reflected from the sample [1-4]. There are, however several instances where these techniques are inadequate even for clear, transparent materials, where one has to measure a very weak absorption. This problem occurs for all forms of matter. Over the years various techniques have been developed to overcome this difficulty, such as derivative spectroscopy, which also seems to be generally inadequate. In addition, there are substances, both organic and inorganic, that are not readily amenable to the conventional transmission or reflection modes of optical spectroscopy. These are usually highly light-scattering materials, such as powders, amorphous solids, gels etc. There are a number of materials that are optically opaque and have dimensions that far exceed the penetration depth of the photons. External parameters such as surface quality, influence of stray light etc have a pronounced effect on the accuracy of the conventional absorption measurements. The situation will be much more worse in the case of solids, powders etc, especially if the sample is highly
scattering or reflecting. In such situations emission measurements are more appropriate and will give more information about the sample. The non-radiative relaxation of photo - excited state usually results in heating of the sample. The liberated heat energy not only carries the information regarding the absorbed energy but contains details regarding the thermal properties of the sample as well. The group of methods based on the measurement of photo induced heating of the sample is called photo thermal (PT) methods [5-7]. The thermalisation of a sample as a result of non-radiative relaxation brings about changes in many parameters such as density, pressure, refractive index, infrared emissions etc. The various effects produced by light induced heating (photo thermal effects) and their detection techniques are given in table-2.1.

Table 2.1 Common detection techniques used in photothermal spectroscopy

<table>
<thead>
<tr>
<th>Thermodynamic Parameter</th>
<th>Measured Property</th>
<th>Detection Technique</th>
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<tbody>
<tr>
<td>Temperature</td>
<td>Temperature</td>
<td>Calorimetry</td>
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<td>Pyroelectric technique</td>
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<td>Infrared Emission</td>
<td>Photothermal Radiometry</td>
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<td>Pressure</td>
<td>Acoustic Wave</td>
<td>Photoacoustic Spectroscopy</td>
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<td>Surface Deflection</td>
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<td>Density</td>
<td>Surface Deformation</td>
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The branch of photothermal spectroscopy based on the pressure wave measurement is known as Photoacoustic (PA) technique [8-21].
During the past four decades, Photoacoustic spectroscopy (PAS) has been developed to study those materials that are unsuitable for the conventional transmission or reflection methodologies. PAS is different from the conventional techniques chiefly in that the interaction of the incident optical photons with the material under investigation is studied through a direct measure of the energy absorbed by the material since the photoacoustic signal generation directly depends on the amount of energy absorbed. The various photothermal methods are depicted in figure 2.1.

![Diagram showing different types of photothermal signal generation](image)

**Fig. 2.1 Different types of photothermal signal generation**

In Photoacoustic Technique, the sample is illuminated by an intensity modulated light source. The modulation can be achieved using
mechanical chopper, acoustoptic modulator, electroptic modulator etc. for continuous wave sources. When the incident photons are absorbed by the sample, internal energy levels within the sample are excited and upon subsequent de-excitation, all or part of the absorbed photon energy is transformed into heat energy through non-radiative de-excitation processes. This periodic heat flow (owing to the periodic excitation by intensity modulation), produces pressure fluctuations resulting in sound or acoustic signal. In gas samples, the detection can be done using a sensitive microphone, whereas in the case of liquid samples the resulting stress signals are detected using piezoelectric detectors. In the case of solid samples, two kinds of detection schemes are possible, viz. indirect detection and direct detection. In the indirect detection, the heat released by the solid sample causes pressure fluctuations in the surrounding air which can be detected by a sensitive microphone. In the direct detection scheme, a piezoelectric detector attached to the sample will measure the stress signal generated as a result of the modulated heating. The signal output from the microphone or the piezoelectric detector can be recorded as a function of the wavelength of light used or as a function of the chopping frequency.

Photoacoustic technique is, much more than just spectroscopy. It can be used to measure the absorption or excitation spectrum, the lifetime of excited states and the energy yield of radiative processes. These are all spectroscopic measurements. On the other hand, it can also be used to measure the thermal properties, thickness of layers and thin films and perform a variety of other non-spectroscopic
investigations. Thus photoacoustic studies can be performed on all types of materials – inorganic, organic and biological and on all states of matter.

2.2 History of Photo Acoustic Effect

The photoacoustic effect in both nongaseous and gaseous matter was discovered by Alexander Graham Bell in the year 1880. He showed that the solar radiation, dispersed with a prism and chopped at an audio frequency is absorbed by different materials to varying amounts depending upon the wavelength, and produced varying audio signals [22,23]. One of the transmitters developed by Bell called photophone consisted of a voice-activated mirror (which was activated by sound waves), a selenium cell and an electrical telephone receiver. The intensity-modulated sunlight was then focused onto a selenium cell. Since electrical resistance of selenium varies with the intensity of light falling on it, the voice-modulated beam of sunlight resulted in electrically reproduced telephonic speech.

Bell demonstrated that the photo acoustic effect in solids was dependent on the absorption of light and that the strength of the acoustic signal was in turn dependent on how strongly the incident light was absorbed by the material. He concluded that “The nature of the rays that produces sonorous effects in different substances depends upon the nature of the substances that are exposed to the beam, and that the sounds in every case are due to those rays of the spectrum that are absorbed by the body”. Bell thus correctly deduced the intrinsic optical absorptive dependence of the photo acoustic effect.
Though Bell had prophesized the scope of his novel observation, after the initial flurry of interest generated by his original work, experiments with the photoacoustic effect remained almost in a dormant state for nearly 50 years. This was mainly because the experiments were difficult to perform since the investigator's ear had to serve as the signal detector. After the advent of microphones, Veingerov of Leningrad was able to observe this effect in gaseous samples. Between 1950 and 1970 the photoacoustic gas analyzer employing a conventional light source gave way to the more sensitive gas chromatographs and the spectrograph was overtaken by the more versatile infrared spectrophotometer. During this period, the photoacoustic effect was primarily employed to study vibrational life times and other aspects of radiation less de-excitation in gases. The advent of lasers in the early 1970's paved a new way in the photoacoustic spectroscopy of gaseous samples. The application of this technique was effectively and efficiently extended to liquids and solids only after the successful formulation of a general theoretical model by Rosencwaig and Gersho (R-G) in the mid seventies [8-10].

Subsequent developments in the theoretical aspects of photothermal phenomena are mere extensions of modifications of R-G model. A modification to the R-G theory by McDonald and Wetsel in 1978 by taking into account the contribution from thermally induced vibrations in the sample is somewhat intriguing. The most widely used model for describing photo acoustic effect in condensed sample in a gas–microphone cell was originally developed by Rosencwaig and
Gersho in 1976[10]. It is valid for acoustic wavelengths much greater than the dimensions of the sample and gas column.

2.3 Photo Induced Processes

The absorption of photons by atoms or molecules will result in a series of processes or effects in a material [5,6]. The excited level may lose its energy by radiative processes, such as spontaneous or stimulated emission, and by non-radiative processes, which mainly results in heat generation. If the photon energy is high enough, direct photochemical changes may take place. Destructive changes may take place at very high power densities of the incident light. A schematic representation of various photo-induced processes and main channels of photo-induced changes that occur in condensed matter is given in the following figure 2.2.

![Schematic representation of photo-induced processes](image)

**Fig 2.2** A Schematic representation of photo-induced processes

In the figure $E_1$ and $E_2$ represent the energies of the lower and upper levels and
$E_2-E_1 = h\nu$ is the energy of the absorbed photon. The absorbed power in the sample $I_{\text{abs}}$ is in accordance with

$$I_{\text{abs}} = I_0 \left[1 - \exp(-\alpha L)\right] \approx \alpha I_0 L$$ .......................... (1)

with $\alpha L \ll 1$. Here $I_0$ and $L$ are the incident light intensity and the sample length respectively and $\alpha$ is the absorption coefficient.

Now, the absorbed energy will be liberated through radiative, nonradiative or chemical processes and each of these processes has specific quantum yield [24].

If $n_r$, $n_{nr}$ and $n_{pc}$ are the quantum yields of radiative, nonradiative and photochemical processes respectively, the total quantum yield of all the channels of de-excitation is given by

$$n_r + n_{nr} + n_{pc} = 1$$ .......................... (2)

Accordingly, the intensity $I_{\text{abs}}$ of the laser radiation, absorbed over all these channels is

$$I_{\text{abs}} = I_r + I_{nr} + I_{pc}$$ .......................... (3)

where $I_r = n_r I_{\text{abs}}$, $I_{nr} = n_{nr} I_{\text{abs}}$ and $I_{pc} = n_{pc} I_{\text{abs}}$ are the amounts of energy liberated through the radiative, nonradiative and photochemical processes respectively.

Measurement of the energy absorbed or that released through any of these relaxation channels facilitates the study of various properties and related parameters of the sample.
2.4 Theory of Photoacoustic Effect by Rosencwaig & Gersho

The Rosencwaig-Gersho theory is a one dimensional heat flow model for the analysis of the production of a photoacoustic signal in a cell [8]. According to R-G theory with gas–microphone detection, the signal depends on the generation of an acoustic pressure disturbance at the solid–gas interface. The generation of the surface pressure disturbance, in turn depends on periodic temperature at the sample-gas interface. The formulation of R-G model is based on the light absorption and thermal wave propagation in an experimental configuration as in figure 2.3. Here a cylindrical cell of length $L$ and diameter $D$ is considered. Assume that the length $L$ is small compared to the wavelength of the acoustic signal. The sample is considered to be in the form of a disk having diameter $D$ and thickness $l$. The sample is mounted so that its front surface is exposed to the gas (air) within the cell and its back surface is a poor thermal conductor of thickness $h$. The length $l_g$ of the gas column in the cell is then given by $l_g = L - l - h$. Further assumption is that the gas and backing materials are not light absorbing. Let $k_i$, $\rho_i$, $C_i$, and $\alpha_i$ represent the thermal conductivity, density, specific heat and thermal diffusivity respectively of the material $i$. Then $a_i = (\rho_i/2\alpha_i)^{1/2}$ is the thermal diffusion co-efficient and $\mu_i = 1/a_i$ is the thermal diffusion length of the material. $i$ can take subscripts $s$, $g$ and $b$ for solid, gas and backing material respectively. $\omega$ denotes the chopping frequency of the incident light beam in radians per second.
Assume that the sinusoidally chopped monochromatic light with wavelength $\lambda$ is incident on the solid with intensity

$$I = (1/2) I_0 (1 + \cos \omega t) \quad \text{(4)}$$

The main source of acoustic signal arises from the periodic heat flow from the solid to the surrounding gas. The periodic heating causes the boundary layer of gas to expand and contract periodically. This can be thought of as the action of an acoustic piston on the rest of the gas column, producing an acoustic pressure signal that travels through the entire gas column. The displacement of the gas piston due to the periodic heating can be estimated using the ideal gas law,

$$\delta x(t) = 2\pi \mu \frac{\phi(t)}{g T_0} = \frac{\theta \mu}{\sqrt{2} T_0} \exp \left[ j \left( \omega t - \frac{\pi}{4} \right) \right] \quad \text{(5)}$$

where the average dc temperature of the gas boundary layer is set as the dc temperature at the solid surface, $T_0 = \phi + \theta_0$, $\phi$ being the ambient temperature at the cell walls. Assuming that the rest of the gas responds to the action of the piston adiabatically, the acoustic pressure in the cell due to the displacement of the gas piston can be obtained from the adiabatic gas law $PV^n = \text{constant}$, where $P$ is the pressure, $V$ is the gas volume in the cell, and $\gamma$ the ratio of the specific heats. Thus the incremental pressure is

$$\delta P(t) = \frac{\gamma P_0}{V_0} \delta V = \frac{\gamma P_0}{l g} \delta x(t) \quad \text{(6)}$$
where $P_0$ and $V_0$ are the ambient pressure and volume respectively and $-\delta V$ is the incremental volume. Then from equations (5) & (6)

$$\delta P(t) = Q \exp \left[ j \left( \omega t - \frac{\pi}{4} \right) \right] \quad \cdots \cdots \cdots \cdots \cdots (7)$$

where $Q = \frac{\gamma P_0 \theta}{\sqrt{2} \pi a g T_0}$

The actual physical pressure variation is given by the real part of $\delta P(t)$ and $Q$ specifies the complex envelope of the sinusoidal pressure variation. The ac temperature distribution $\theta$ is calculated by solving the heat diffusion equations. Rosencwaig and Gersho solved the one dimensional heat diffusion equations assuming no lateral heat flow.

The one dimensional heat diffusion equations in the three regions can be written as

\begin{align*}
\frac{\partial^2 \varphi_b}{\partial t^2} &= \frac{1}{\alpha_b} \frac{\partial \varphi_b}{\partial t}, \quad -l-l_b \leq x \leq -l \quad \text{Region III} \quad \cdots \cdots \cdots \cdots \cdots (i)
\end{align*}
\[
\frac{\partial^2 \varphi_g}{\partial t^2} = \frac{1}{\alpha_g} \frac{\partial \varphi_g}{\partial t}, \quad 0 \leq x \leq -l_g \quad \text{Region I} \quad \text{................. (ii)}
\]

\[
\frac{\partial^2 \varphi_s}{\partial t^2} = \frac{1}{\alpha_s} \frac{\partial \varphi_s}{\partial t} - A \exp(\beta x)[1 + \exp(j \omega t)], \quad -l \leq x \leq 0 \quad \text{Region II} \quad \text{...(iii)}
\]

where \( A = \frac{\beta l_0 \eta}{2k_s} \)

Here \( \varphi \) is the temperature and \( \eta \) is the light conversion efficiency. The real part of the complex-valued solution \( \varphi(x, t) \) of the above equations is the solution of physical interest and represents the temperature in the cell relative to the ambient temperature as a function of position and time. Thus, the actual temperature field in the cell is given by

\[
T(x, t) = \text{Re}[\varphi(x, t)] + \phi
\]

where \( \text{Re} \) denotes "the real part of " and \( \phi \) is the ambient (room) temperature.

The complex amplitude of the periodic temperature distribution, \( \theta \) at the solid-gas boundary (\( x=0 \)) is given by

\[
\theta = \frac{\beta l_0}{2k_s(\beta^2 - \sigma_s^2)} \left( \frac{(r-1)(b+1)\exp[\sigma_s l] - (r+1)(b-1)\exp[-\sigma_s l] + 2(b-r)\exp(-\beta l)}{(g+1)(b+1)\exp[\sigma_s l] - (g-1)(b-1)\exp[-\sigma_s l]} \right) \quad \text{...(iv)}
\]

where \( b = \frac{k_b a_b}{k_s a_s} \), \( g = \frac{k_g a_g}{k_s a_s} \), \( r = (1 - j) \frac{\beta}{2a_s} \) and \( \sigma_s = (1 + j)a_s \).
Substituting for $Q$,

$$Q = \frac{\beta_{0}P_{0}}{2\sqrt{2k_{s}/g}a_{g}T_{0}\left(\beta^{2} - \sigma_{s}^{2}\right)} X$$

$$\left(\frac{(r-1)(b+1)\exp\left(\sigma_{s}l\right) - (r+1)(b-1)\exp\left(-\sigma_{s}l\right) + 2(b-r)\exp(-\beta l)}{(g+1)(b+1)\exp\left(\sigma_{s}l\right) - (g-1)(b-1)\exp\left(-\sigma_{s}l\right)}\right)$$

Thus, equation (8) can be used to evaluate the amplitude and phase of the acoustic pressure wave produced in the cell by photoacoustic effect. It can be observed that interpretation of the full expression for $\delta P(t)$ is difficult because of the complex expression of $Q$. Some physical insight can be gained if certain special cases according to the optical opaqueness of solids are examined. For each category of optical opaqueness, three cases according to the relative magnitude of the thermal diffusion length $\mu_{s}$, as compared to the physical length $l$ and the optical absorption length $\mu_{\beta}$ can be considered.

Defining, $Y = \frac{\gamma P_{0}I_{0}}{2\sqrt{2l/g}T_{0}}$, ................................ (9)

CASE I: Optically Transparent Solids ($\mu_{\beta} > 1$)

1. **Case Ia: Thermally Thin Solids ($\mu_{s} >> l$ ; $\mu_{s} >> \mu_{\beta}$)**

We can set $e^{\beta l} \approx 1 - \beta l$, $e^{\kappa \sigma l} \approx 1$ and $|\tau| > 1$ in equation (8) and hence we obtain

$$Q = \frac{(1-i)\beta l}{2a_{g}} \left(\frac{\mu_{b}}{k_{b}}\right) Y$$

................................ (10)
Thus the acoustic signal is proportional to $\beta l$ and varies as $f^1$. In addition, the thermal properties of the backing material come into play in the expression for $Q$.

2. **Case Ib: Thermally Thin Solids ($\mu_s > 1$; $\mu_s < \mu_B$)**

Here we can set $\exp(-\beta l) \equiv 1-\beta l$, $e^{\pm\sigma l} \equiv 1 \pm \sigma l$ and $|r| < 1$ in equation (8).

\[
Q = \frac{(1-j)\beta l \left( \frac{\mu_B}{k_B} \right)}{2a_g} Y \quad \text{.................................. (11)}
\]

This equation is identical with equation (10) and hence the acoustic signal behaves in the same fashion.

3. **Case Ic: Thermally Thick Solids ($\mu_s > 1$; $\mu_s << \mu_B$)**

In this case we set $\exp(-\beta l) \equiv 1-\beta l$, $e^{\pm\sigma l} \equiv 0$ and $|r| << 1$ in equation (8)

\[
Q = -j \frac{\beta l}{2a_g} \left( \frac{\mu_s}{k_s} \right) Y \quad \text{.................................. (12)}
\]

The acoustic signal is now proportional to $\beta \mu_s$ rather than $\beta l$. This means that light absorbed within the first thermal diffusion length contributes to the signal, although light is being absorbed throughout the length of the solid. Moreover, $\mu_s$ being less than the thickness $l$, thermal properties of the backing material will not influence the signal. Here the signal varies as $f^{-3/2}$ with the modulation frequency.
CASE II: Optically Opaque Solids

Case II a: Thermally Thin Solids ($\mu_s > 1 ; \mu_s > \mu_\beta$)

In equation (8), we set $\exp(-\beta l) \approx 0$, $e^{+\alpha l} \approx 1$ and $|r| >> 1$

Then we obtain

$$Q = \frac{(1-j)}{2a_g} \begin{pmatrix} \mu_b \\ k_b \end{pmatrix} Y$$

...........................................(13)

Here the photoacoustic signal is independent of $\beta$, which is valid for a perfect black absorber. The signal depends on the thermal properties of the backing material and varies as $1/f$.

Case II b: Thermally Thick Solids ($\mu_s < 1 ; \mu_s > \mu_\beta$)

We set $\exp(-\beta l) \approx 0$, $e^{+\alpha l} \approx 0$ and $|r| > 1$ in equation (8)

We obtain

$$Q = \frac{(1-j)}{2a_g} \begin{pmatrix} \mu_s \\ k_s \end{pmatrix} Y$$

...........................................(14)

Though equations (13) & (14) are similar, in the present case there is no contribution from the thermal properties of the backing material.

Case II c: Thermally Thick Solids ($\mu_s << 1 ; \mu_s < \mu_\beta$)

We set $\exp(-\beta l) \approx 0$, $e^{+\alpha l} \approx 0$ and $|r| < 1$ in equation (8). Then we obtain

$$Q = \frac{-j \beta \mu_s}{2a_g} \begin{pmatrix} \mu_s \\ k_s \end{pmatrix} Y$$

...........................................(15)
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The photo acoustic signal will be proportional to $\beta \mu_s$. The signal is independent of the thermal properties of the backing material and varies as $f^{3/2}$. A theoretical analysis of the photoacoustic effect applied to different cases has been discussed and can be applied to the study of any kind of sample.

The photo acoustic measurements can be done in two different configurations (1) by heat reflection configuration and (2) by heat transmission. The photo acoustic cell can be designed for the two configurations. In the reflection configuration, the microphone is situated above the sample surface. Hence the temperature distribution at $x = 0$ is to be determined. In the case of heat transmission configuration, the temperature distribution at $x = -1$ has to be determined as the microphone is situated below the sample. In the above theoretical description, $x = 0$ case is solved and the different expressions for special cases are obtained for this particular case. For the heat transmission case, the expressions for the special cases will be different as the temperature distribution corresponding to $x = -1$ will be used in the calculations.

The above analysis is based on the assumption of no lateral heat flow. However, if there exists a lateral heat flow, then three dimensional heat diffusion equations have to be solved for obtaining the temperature distribution.

The heat diffusion equations in the three layers can be written as
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\[
\frac{\partial^2 T_g}{\partial r^2} + \frac{1}{r} \frac{\partial T_g}{\partial r} + \frac{\partial^2 T_g}{\partial z^2} = \frac{1}{\alpha_g} \frac{\partial T_g}{\partial t}
\] ............................... (1a)

for the gas in front of the sample with \( \alpha_g \) being the thermal diffusivity of air (gas).

\[
\frac{\partial^2 T_s}{\partial r^2} + \frac{1}{r} \frac{\partial T_s}{\partial r} + \frac{\partial^2 T_s}{\partial z^2} = \frac{1}{\alpha_s} \frac{\partial T_s}{\partial t} - \frac{Q}{k_s}
\] ............................... (1b)

where the second term on the right hand side represents the source term as the sample absorbs light and acts as the source of heat with \( Q = \frac{I_0 \eta}{2} \beta \exp(-\beta x)(1+\exp(j \omega t)) \). \( \eta \) is the light to heat conversion efficiency, \( \beta \) the absorption coefficient at the excitation wavelength, \( k_s \) is the thermal conductivity of the sample and \( \alpha_s \) is the thermal diffusivity of the sample.

\[
\frac{\partial^2 T_g}{\partial r^2} + \frac{1}{r} \frac{\partial T_g}{\partial r} + \frac{\partial^2 T_g}{\partial z^2} = \frac{1}{\alpha_g} \frac{\partial T_g}{\partial t}
\] ............................... (1c)

for the backing (air).

The boundary conditions are

\[ T_g(z = 0, t) = T_s(z = 0, t) , \]

\[ k_s \frac{\partial T_s(z = 0, t)}{\partial z} = k_g \frac{\partial T_g(z = 0, t)}{\partial z} \]
\[ T_g(z = -l, t) = T_s(z = -l, t), \]
\[ k_s \frac{\partial T_s(z = -l, t)}{\partial z} = k_g \frac{\partial T_g(z = -l, t)}{\partial z} \]
\[ T_g(z = \infty, t) = T_g(-\infty, t) = 0 \]

If the heating beam is Gaussian of power \( P \) and \( 1/e^2 \) radius is ‘a’ then the source term \( Q \) can be written
\[ Q(r, z, t) = \frac{\beta P \eta}{\pi a^2} \exp \left( -\frac{2r^2}{a^2} \right) \exp(\beta z)(1 + \exp(j\omega t)) \]

### 2.5 Thermal Diffusivity Measurement using Photoacoustic Technique

#### 2.5.1 Heat Conduction in Solids

Heat conduction is a process in which heat is transferred from one part of the sample to another as a result of a temperature gradient. Mainly there are two mechanisms by which thermal transport is taking place in a solid [24-27].

a. The heat conduction due to charge carrier motion which is termed as electron or hole heat conductivity \( (k_e) \) and

b. The heat conduction due to lattice vibrations or phonons \( (k_l) \)

When a temperature gradient is built up in a substance the energy gradient is transmitted in such a manner that energy is transmitted from an atom, which oscillates with more intensity to an atom which oscillates with less intensity.
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The total heat conductivity $k = k_e + k_l$

In this $k_l$ is related to the elastic properties of the solid and $k_e$ to the charge carrier concentration. In metals $k_e \gg k_l$ and in dielectrics $k_l \gg k_e$. In semiconductors $k_e$ strongly depends on the composition and on the temperature.

When a semiconductor is irradiated with an optical radiation of suitable energy, in addition, photo generated carrier recombination will also contribute to the heat transport. Free carrier generation resulting from the light absorption occurs when the incident photon energy is greater than the band gap energy. The photon is absorbed in this process and excess energy $E_{ph} - E_g$ is added to the electron and hole in the form of kinetic energy. Now the non-radiative recombination of these carriers will result in the form of heat to the lattice [12,13]. Another form of non-radiative recombination process is the surface recombination. Surfaces and interfaces of semiconductors usually contain a large number of recombination centers because of the abrupt termination of the crystal, which leaves a large number of electrically active dangling bonds. In addition, surfaces and interfaces are likely to contain more impurities. The surface recombination is also an interband recombination process and excess energy is ultimately transferred to the lattice as heat. Trap assisted recombination is also one among the recombination mechanisms. Apart from this there exists an instantaneous thermalisation component, which arises from intra band interaction of excited electrons with the lattice. This process is an after effect of excitation of electrons to the higher levels in the conduction
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band. Such hot electrons will come back to the minimum of the conduction band by imparting the excess energy to the lattice. This thermalisation takes place in pico seconds and hence is known as instantaneous thermalisation.

2.6 Thermal Conduction by Phonons

The transmission of heat can be conveniently explained by considering phonon gas transport. In every region of space there are phonons traveling in all directions, much like the molecules in a gas. The advantage of using this gas model is that many of the concepts of the kinetic theory of gases can also be applied here. The thermal conductivity is given by

\[ k = \frac{cvl_m}{3} \]

where \( c \) is the specific heat per unit volume, \( v \) is the speed of the particle, and \( l_m \) is its mean free path [26]. The only difference in solids is that phonons replace the molecules so that the velocity and mean free path now refer to phonons instead of gas molecules. The thermal conductivity \( k \) will be determined by the nature of the mean free path, since \( c \) is constant at high temperatures and varies as \( T^3 \) at low temperatures and \( v \) is almost a constant. Here \( l_m \) is the average distance the phonon travels between two successive collisions. This in turn is determined by the scattering mechanisms. The important scattering mechanisms are (1) scattering due to phonon-phonon interaction (2) scattering by imperfections such as impurities and dislocations and (3) boundary scattering caused by collision of phonons with the external boundaries of the sample.
The phonon-phonon collision becomes more pronounced at high temperatures, at which the atomic displacements are large and this gives rise to harmonic coupling between phonons, causing their mutual scattering. In this region the mean free path is inversely proportional to the temperature \( l_m \propto 1/T \). This is reasonable, since the larger the value of \( T \), the greater is the number of phonons participating in the collision process.

Crystal imperfections such as impurities and defects also can scatter phonons because they partially destroy the perfect periodicity, which is the very basis of the concept of a freely propagating lattice wave. This scattering may be due to (1) point defects and/or due to (2) dislocations. Thus the random distribution of different isotopes leads to a decrease in thermal conductivity. For instance a substitution point impurity having a mass different from that of the host atom causes scattering of the wave at the impurity. The greater the difference in mass and the density of impurities, the greater is the scattering and the shorter the mean free path. This gives rise to a decrease in the value of thermal conductivity there by reducing the thermal diffusivity of the sample.

Though various techniques are available for the measurement, the photo acoustic technique has proved to be the most efficient and convenient tool for the measurement of thermal diffusivity. The detected signal is strongly dependent upon the interplay of the sample’s optical absorption coefficient for the incident radiation, the light into heat conversion efficiency, as well as how heat
diffuses through the sample. The dependence of the photo acoustic signal on the absorption coefficient allows one to perform spectroscopic studies, where as the fact that the signal is proportional to the light into heat conversion efficiency means that it is complementary to other photo induced energy conversion processes. Thus the photo acoustic signal can be used for obtaining the information concerning the non-radiative de-excitation processes.

2.7 Significance of Thermal Diffusivity Measurement

The photoacoustic process depends not only on the optical properties of the sample but on its thermal and geometric parameters and in some cases on its elastic properties as well. The thermal diffusivity $\alpha$ is of direct importance in heat flow studies as it determines the rate of periodic or transient heat propagation through a medium.

Jean Fourier has derived the basic law defining the propagation of heat in a one-dimensional homogeneous solid as [26-30].

$$\frac{\partial Q}{\partial t} = -kA\frac{\partial T}{\partial x} \quad \text{this is known as Fourier equation.}$$

This equation implies that the quantity of heat $\partial Q$ conducted in the X–direction of a uniform solid in time $\partial t$ is equal to the product of the conducting area $A$ normal to the flow path, the temperature gradient $\partial T/\partial x$ along the path and thermal conductivity $k$ of the material.
Chapter 2

Formal definition of thermal diffusivity arises when deriving an expression for a transient temperature field in a conducting solid from Fourier equation. The equation describing the temperature field in a homogeneous, linear conducting solid with no internal heat source is

$$\nabla^2 T = 1/\alpha \frac{\partial T}{\partial t}$$

Here $\alpha$ is the thermal diffusivity, which is related to the thermal conductivity ($k$), density ($\rho$) and specific heat capacity ($c$) of the material as

$$\alpha = \frac{k}{\rho c}$$

The thermal diffusivity $\alpha$ is expressed in $m^2/s$. Because of its controlling effect and common occurrence in heat flow problems, its determination is often necessary and knowledge of the thermal diffusivity can in turn be used to calculate the thermal conductivity. Changes in the thermal parameters such as thermal conductivity can be used to monitor changes within a material. The significance of $\alpha$ is evident from the above relationship. The reciprocal $1/\alpha$ expressed in $sm^{-2}$ is a measure of the time required to heat up a material to some temperature level. Therefore, the ratio of heating times for two materials of the same thickness will be inversely proportional to the thermal diffusivity values. Thus $\alpha$ is a significant thermodynamic parameter that determines the heat diffusion in bulk as well as thin film samples.
Fig. 2.4 Schematic diagram of the PA experimental arrangement

2.8 Density Functional Theory

The analysis of the PA spectra is based on Density Functional Theory and its approximations for prediction of electronic band structure. Density functional theory is one of the most popular and powerful quantum mechanical approaches to matter and is being successfully applied for the calculation of band structure of solids, binding energy of molecules etc. It is highly versatile owing to the generality in its fundamental concepts and the flexibility in implementing them. The two core elements of DFT are Hohenberg-Kohn (HK) theorem and the Kohn-Sham (KS) equations [31-34]. The HK theorem states that given a ground state density \( n_0 (r) \) it is possible to calculate the corresponding ground state wave function
\( \psi_0(r_1, r_2, \ldots r_N) \). This means that \( \psi_0 \) is a functional of \( n_0 \) and hence all the ground state observables are functional of \( n_0 \) too. The ground state wave function should also minimize the energy and for a ground state density \( n_0(r) \), this requirement can be written as

\[
E_{v,0} = \min_{\Psi \rightarrow n_0} \langle \Psi | \hat{T} + \hat{U} + \hat{V} | \Psi \rangle ,
\]

where \( E_{v,0} \) denotes the ground state energy in potential \( v(r) \). This implies that for a given density \( n_0(r) \), the ground state wave function \( \psi_0 \) is that which reproduces this \( n_0 \) and minimizes energy. If the density is different from the ground state density \( n_0(r) \), then the wave functions \( \psi \) that produce this density \( n \) are different from the ground state wave function \( \psi_0 \). In this case the functional can be defined as

\[
E_v[n] = \min_{\Psi \rightarrow n} \langle \Psi | \hat{T} + \hat{U} + \hat{V} | \Psi \rangle .
\]

The functional \( E_v[n] \) is minimized by the ground state density \( n_0 \) and its value at minimum is \( E_{v,0} \). In the Kohn Sham approach, it does not work exclusively in terms of particle density but with special kind of wave functions (single particle orbital). Though DFT will look like a single particle theory, many body effects will be included via the so-called exchange correlation functional. With the exchange correlation functional, the energy functional can be written as

\[
\]

The kinetic energy functional \( T[n] \) is decomposed into a part representing kinetic energy of non-interacting particles of density \( n \), \( T_s[n] \) and the remainder is \( T_c[n] \) where \( c \) represents correlation and \( s \) represents single particle. \( U_H \) is the Hartree energy and \( \phi \) is the Kohn
Sham orbital. $E_{xc}$ contains the differences between $T-T_s$ and $U-U_H$. $E_{xc}$ is known as the exchange correlation energy and is often decomposed into $E_x + E_c$, where $E_x$ is due to Pauli's principle and $E_c$ is due to the correlations.

There are basically three distinct types of approximations involved in a DFT calculation. The first one is the interpretation of the KS eigenvalues and orbitals as physical energies and wave functions. The second approach is numerical and concerns methods for actually solving the differential equation where the major problem arises in the selection, of the suitable basis functions. There is a fundamental dichotomy between the methods that work with the fixed basis functions that do not depend on the energy and methods that employ energy dependent basis functions. Fixed basis functions are used in plane wave expansions, linear combination of atomic orbitals (LCAO) approximations, orthogonalized plane wave etc and methods using energy dependent functions are the APW (augmented plane wave) or the Korringa/Kohn/Rostoker [35,36] approaches. However, this distinction becomes less clear-cut with the linear methods in which the energy dependent basis functions are linearized around some fixed reference energy like in Linear Muffin Tin Orbital method (LMTO) [37-40] and Linear Augmented Plane waves approach (LAPW)[40-43]. The third type of approximation involves constructing an expression for the exchange correlation energy functional $E_{xc}[n]$ which contains the many body aspects of the problem. There exists different functional for the local functional, Thomas-Fermi approximation (TF) [44] Local
Density Approximation [LDA][32], Local Spin Density Approximation [45] etc, semi local or gradient functional [Generalized Gradient Approximation (GGA)[46] and Gradient Expansion Approximation (GEA)[47], non local functional (hybrids, orbital functional such as meta-GGA, EXX and SIC and integral dependent functions such as ADA [34].

2.9 Electrical Properties of Polycrystalline Materials

Electrical conductivity measurements are extensively used for investigating the mechanism of charge transport in materials in addition to probing structural defects and internal purity of crystalline solids. The investigations carried out till date on a variety of materials describe their electrical conductivity in terms of electrons/holes, ions, polarons, impurities, defects, vacancies etc. Most of the battery materials available show special property of storing and dissipating electrical energy when subjected to electric fields. In the case of materials of interest in the present work, LiMPO₄ (M=Fe, Mn, Ni, Co) olivine phosphates, it has been recently reported that the electron transport mechanism is by means of small polarons [48]. The concept of small polaron model has been detailed in several articles [49,50]. When charge carriers like electrons or holes are present in a polar crystal, the atoms in their environment will be polarized and displaced and produce a local lattice distortion. The ion displacement becomes more pronounced as the charge carriers become more and more localized. The carrier lowers its energy by localizing into such a lattice deformation and becomes self trapped. This quasi particle formed by
the electron and its self-induced distortion is called a small polaron if
the range of lattice distortion is of the order of lattice constant. These
charge carriers can be either electrons or holes in LiMPO₄. Since the
hopping process dominates the electrical transport in this material, the
dielectric measurements will provide a useful knowledge on the
polaron dynamics because a hopping process of polarons has a high
probability of involving a dielectric relaxation that contains several
significant parameters in the elucidation of the polaron dynamics [51].

2.10 AC Conductivity

The theory involved for the evaluation of a.c conductivity from
dielectric constant values is as follows. Any capacitor when charged under
a voltage will have some loss current due to ohmic resistance or
impedance by heat diffusion [52]. For a parallel plate capacitor of area of
cross-section A and plate separation d the a.c conductivity is given by

$$\sigma_{ac} = \frac{J}{E}$$ ........................................ (1)

where J is the current density and E is the electric field intensity. But
the electric field vector is related to the displacement vector D of dipole
charges and the complex permittivity of the material $\varepsilon$ as

$$E = \frac{D}{\varepsilon}$$ ........................................ (2)

For a parallel plate capacitor the electric field vector E is related to the
applied a.c voltage $V = V_0 \exp(j\omega t)$ as
Since the current density \( J = \frac{dq}{dt} \) where \( q = \frac{Q}{A} = \frac{Vc}{d} \) (provided by Maxwell's equation), where \( Q \) is the charge in coulombs due to a potential difference \( V \) volts between the capacitor plates. Hence,

\[
J = \frac{dq}{dt} = \frac{d}{dt} \left( \frac{Vc}{d} \right) = \frac{\varepsilon}{d} \frac{dV}{dt} = \frac{\varepsilon}{d} Vj\omega
\]

Substituting for \( E \) and \( J \) from equations (2) and (4) we get

\[
\sigma_{ac} = \varepsilon j\omega
\]

Since permittivity is a complex quantity, it can be written as \( \varepsilon = \varepsilon' - j\varepsilon'' \) then

\[
\sigma_{ac} = j\omega \left( \varepsilon' - j\varepsilon'' \right) = j\omega\varepsilon' + \omega\varepsilon''
\]

Neglecting the imaginary term in the conductivity equation we can write

\[
\sigma_{ac} = \varepsilon'' \omega
\]

In a dielectric material there will be some power loss because of work done to overcome the frictional damping forces encountered by the dipoles during their rotation. In an ideal case of a.c field the charging current \( I_C \) and loss current \( I_L \) will be 90° out of phase with the voltage. But in most of the capacitors due to the absorption of electrical energy some loss current, \( I_L \) will also be produced, which will be in
phase with the voltage [52,53]. Charging current, $I_c$, and loss current, $I_L$, will make angles $\delta$ and $\theta$ respectively with the total current $I$.

![Vector diagram of current component](image)

**Fig. 2.5** Vector diagram of current component

Generally, $\sin \delta$ is called the loss factor but when $\delta$ is small then $\sin \delta = \delta = \tan \delta$. But the two components $\varepsilon'$ and $\varepsilon''$ of the complex dielectric constant, $\varepsilon$, are frequency dependent and given by

$$\varepsilon' = D_0 \frac{\cos \delta}{E_0} \hspace{2cm} (8)$$

$$\varepsilon'' = D_0 \frac{\sin \delta}{E_0} \hspace{2cm} (9)$$

From equations (8) and (9) we obtain the loss factor as

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \hspace{2cm} (10)$$

From equation (10) and (7) we modify the expression for a.c conductivity as

$$\sigma_{ac} = \omega \tan \delta \varepsilon' \hspace{2cm} (11)$$
If $f$ is the frequency of the applied field, $\varepsilon_r$ the relative permittivity of the material and $\varepsilon_0$ the permittivity of free space, then $\omega = 2\pi f$, and $\varepsilon' = \varepsilon_0\varepsilon_r$.

Hence from the dielectric loss and dielectric constant, a.c conductivity of the samples can be evaluated using the relation

$$\sigma_{ac} = 2\pi f \tan\delta \varepsilon_0 \varepsilon_r$$

.............................. (12)

Considerable progress has been made by Cole and Cole in utilizing complex plots to explain the dielectric behavior and carrier transport mechanisms in a wide range of solid state materials [52,54,55]. The ac conductivity of a material depends on the dielectric property as well as its capacitance. The variation of ac conductivity with frequency indicates its dispersion, which is attributed to the presence of space charge in material. The behavior of ac conductivity is expressed on the basis of Jonscher’s universal power law [56].

$$\sigma(\omega) = \sigma_{dc} \left[ 1 + \left( \frac{\omega}{\omega_H} \right)^n \right]$$

where $\sigma_{dc}$ is frequency independent part appearing at high frequency and $\omega_H$ corresponds to the crossover frequency separating dc regime from the dispersive conduction (hopping frequency) and the frequency exponent $n$ lies between 0 and 1. The ac activation energy can be obtained by plotting the hopping frequency $\omega_H$ and temperature using the relation,

$$\omega_H = \omega_0 \exp\left( -\frac{E_H}{kT} \right).$$
2.11 DC Conductivity

By Ohm's law, $V = IR$ where $V$ is the voltage, $I$ the current and $R$ the resistance. $V = EL$ where $E$ is the electric field and $L$ the length and $I = JA$ where $J$ is the current density and $A$ the area of cross section. Hence, $E = \frac{JAR}{L} = J\rho$, where $\rho$ is the resistivity. In other words, $J = \frac{E}{\rho} = \sigma E$, where $\sigma$ is the dc electrical conductivity. The dc conductivity measured as a function of the temperature can lead to the information regarding the activation energy from the Arrhenius relation

$$\sigma(T) = \frac{\sigma_0}{T} \exp\left(-\frac{E_a}{kT}\right)$$

where $E_a$ is the activation energy and $T$ the temperature.

2.12 X-Ray Diffraction Analysis

According to Bragg, X-rays behave as if they are reflected by planes of atoms in a crystal and when a beam of X-rays is allowed to fall on a crystal surface at some angle $\theta$, each atom there in acts as a source of scattered radiation of the same wavelength. Thus when X-ray beam strikes a crystal surface at an angle $\theta$, a portion is scattered by the layer of atoms at the surface and the unscattered portion of the beam penetrates to the second layer of the atoms, where again a fraction is scattered and the remainder passes on to the third layer. The cumulative effect of this scattering from the regularly spaced centers of the crystal is nothing but diffraction of the beam, which is almost similar to diffraction of visible radiation by a reflection grating.
William Henry Bragg and his son William Lawrence Bragg developed a useful relationship between the wavelength of X-rays and the spacing between the lattice planes. As the atoms in a crystal are orderly arranged, a beam of X-rays can be reflected from a plane of atoms similar to the reflection of light from a plane mirror [57,58].

The most important requirements of diffraction are

a. The spacing between the layers of atoms must be roughly the same as the wavelength of radiation

b. The scattering centers must be distributed in a highly regular manner.

By considering a beam of monochromatic X-rays which strikes a set of parallel and equidistant planes called lattice planes or Bragg’s planes in the crystal structure at an angle \( \theta \) (glancing angle) scattering occurs as a result of interaction of radiation with atoms located at different points at various planes. Bragg obtained a formula given by,
2d_{hkl} \sin \theta = n \lambda

where \( n \) is the order of reflection \( d_{hkl} \) the inter-planar distance of the crystal and \( \lambda \) the wavelength of X-ray used.

The X-ray diffraction technique can be conveniently employed for the identification and characterization of solids. For elements and compounds, crystallizing in the simple crystal systems such as cubic, tetragonal, hexagonal etc., the Bragg’s law enables determination of unit cell parameters with relative ease.

In the X-ray diffractometer, the X-ray source, the specimen and the detector are so arranged to obey Bragg’s law. In our set-up (model 1710 Rigaku), filtered copper \( k_\alpha \) radiation is used for diffraction. The wavelength of radiation is 1.5414 \( \text{Å} \). The accelerating potential applied to the X-ray tube is 30kV and the tube current is 20mA. The sample can be scanned from 0° to 90° and the X-ray diffraction pattern (intensity of diffracted beam versus 2\( \theta \)) of the sample can be recorded.

### 2.13 Scherrer Formula

The powder method is a widely used experimental technique for the determination of grain size. Here we make use of the Scherrer formula given by,

\[
t = 0.9 \lambda / \beta \cos \theta
\]

where \( \beta \) is the full width at half maximum (FWHM) of the most intense diffraction peak and \( \theta \), the corresponding angle.
The basic principle underlying the powder technique is that, since millions of tiny crystals in the powder have completely random orientations, all possible diffractions will be available for Bragg reflection to take place [57,58]. Such reflections will take place from many sets of parallel planes lying at different angles to the incident X-ray beam. Moreover; each set will give not only first order reflections but higher order reflections as well. Since all orientations are equally possible, the reflected rays will form a cone whose axis lies along the direction of the incident beam and whose semi vertical angle is twice the glancing angle for that particular set of planes. For each set of planes, and for each order, there will be such a cone of reflected X-rays. Their intersections with a photographic film set with its plane normal to the incident beam form a series of concentric circular rings. Radii of these circular rings are recorded and the film can be used to find the glancing angle and hence the inter-planar spacing of the crystalline substance.

In the powder method the intensity of the reflected beam can also be recorded in a diffractometer, which uses a counter in place of the film to measure intensities. The counter moves along the periphery of the cylinder and records the reflected intensities against 2θ. Peaks in the diffractometer reading correspond to positions where the Bragg condition is satisfied. From the XRD pattern of the powder sample we can calculate the lattice parameter using the formula 

$$d_{hkl} = \frac{\lambda}{2 \sin \theta}$$
and cubic lattice constant

\[ a = d_{ht} \sqrt{h^2 + k^2 + l^2} \]

The porosity of the samples can be calculated as

\[ \text{Porosity} = \frac{X - \text{Ray density} - \text{apparent density}}{X - \text{Ray density}} \]

Where X-ray density = \( n \) (Molecular Mass / \( N \)) (1/Volume of unit cell)

\( n \) = number of molecules per unit cell.

\( N \) = Avogadro number.

2.14 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) provides a means to investigate the surface morphology of the sample. The SEM is a microscope that uses electrons instead of light to form an image. It provides a high resolution and depth of the field images of the sample surface (so closely spaced specimens can be magnified at much higher levels). The SEM has allowed researchers to examine a much bigger variety of specimens.
The scanning electron microscope has many advantages over traditional microscopes. The two main improvements over conventional optical microscopes are (i) it can magnify a sample up to $x10^5$ and (ii) it improves the depth of field resolution by a factor around 300. Because the SEM uses electromagnets rather than lenses, the researcher has much more control in the degree of magnification [59]. All of these advantages, as well as the actual strikingly clear images, make the scanning electron microscope one of the most useful instruments in research today.
The sample is placed inside the microscope's vacuum column through an air-tight door using a load lock facility. Air is pumped out of the column using a combination of different pumps like rotary, turbo molecular or diffusion pumps. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within the vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample. Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television. This produces the final image. A schematic diagram of SEM is shown in figure 2.7.

2.14.1 Sample Preparation for SEM

Because the SEM utilizes vacuum conditions and uses electrons to form an image, special preparations must be done to the sample. All water must be removed from the samples because the water would
vaporize in the vacuum. All metals are conductive and require no preparation before being used. All non-metals and insulator samples should be coated with gold in order to improve the surface conductivity. This prevents the accumulation of negative surface charges, which might interact with the secondary electron. This process is carried out using a device called a "sputter coater". The sputter coater uses an electric field and argon gas. The sample is placed in a small chamber that is at a vacuum. Argon gas and an electric field cause an electron to be removed from the argon, making the atoms positively charged. The argon ions then become attracted to a negatively charged gold foil. The argon ions knock gold atoms from the surface of the gold foil. These gold atoms fall and settle onto the surface of the sample producing a thin gold coating.

2.15 Transmission Electron Microscopy (TEM)

Transmission electron microscopy was originally used for highly magnified sample images. Later, analytical capabilities such as electron energy loss detectors and light and X-ray detectors were added to the instrument and the technique is now known as analytical transmission electron microscopy (AEM). Transmission electron microscopes are, in principle, similar to optical microscopes; both contain a series of lenses to magnify the sample. The main strength of TEM lies in its extremely high resolution [59,60].

Transmission electron microscopy is a microscopy technique whereby a beam of electrons is transmitted through thin specimen, which interacts with the specimen as it passes through it. An image is
formed from the electrons transmitted through the specimen, magnified and focused by an objective lens and appears on an imaging screen, a fluorescent screen in most TEMs, plus a monitor, or on a layer of photographic film, or to be detected by a sensor such as CCD camera.

Fig. 2.9 Schematic diagram of transmission electron microscope.

Electrons are usually generated in an electron microscope by thermionic emission from a filament, usually tungsten, or by field emission [59,60]. The electrons are then accelerated by an electric potential (usually 100-400kV) and focused by electrostatic and electromagnetic lenses onto the sample. The beam interacts variously with the sample due to differences in density or chemistry. The
transmitted and forward scattered electrons form a diffraction pattern in the back focal plane and a magnified image in the image plane. The beam that is transmitted through the sample contains information about these differences, and this information in the beam of electrons is used to form an image of the sample. The electrons that remain in the beam can be detected using a photographic film, or fluorescent screen. So areas where electrons have been scattered in the sample can appear dark on the screen, or on a positive image due to this scattering.

The three primary imaging modes are bright-field, dark-field, and high-resolution microscopy. Image contrast does not depend very much on absorption, as it does in optical transmission microscopy, but rather on scattering and diffraction of electrons in the sample. Images formed by transmitted electrons are bright-field images and images formed using a specific diffracted beam are dark-field images. Few electrons are absorbed in the sample. These electrons lead to sample heating. A stationary, parallel and coherent electron beam passes through the sample in TEM forming a magnified image in the image plane, which is then simply projected on to the fluorescent screen.

References


Theoretical Aspects


Theoretical Aspects


