# MATERIALS AND METHODS

# CHAPTER III

# MATERIALS AND METHODS

In this chapter, the materials used for the preparation of $TiO_2$ thin film and the methods adopted for the deposition of $TiO_2$ thin film and its characterization are discussed. The preparation of dye-sensitized $TiO_2$ thin film and its characterizations are discussed.

## 3.1 MATERIALS USED

The materials used for the deposition of $TiO_2$ thin film are as follows.

### CHEMICALS

- Titanium tri chloride (Sigma Aldrich)
- Ammonia solution (Loba)
- Hydrochloric acid (Merck)
- Nitric acid (Merck)
- Extran (Merck)
- Deionised water
- Ethanol

### GLASSWARE

- 50 ml beakers
- 250 ml beakers
- 500 ml beakers
- Glass rod
- Measuring jar
- Desiccators
- Microscope slide

## 3.2 DEPOSITION OF $TiO_2$ THIN FILM

- Substrate cleaning.

- Film deposition.

### 3.2.1 CHOICE OF THE SUBSTRATE

The substrates have a pronounced influence on the growth and orientation of the film. In general, the substrate has to be optically planned, transparent, chemically stable, electrically non-interfering and amenable to moderately high temperature before and after deposition of films. Glazed substrates surface provide good surface finish, low porosity and have a low dielectric constant value and are effective for most thin film deposition techniques with relatively low deposition temperature

### 3.2.2 REQUIREMENTS OF SUBSTRATE

The characteristics of the substrate used for defect- free films are given below [58].

- Good surface smoothness
- Good mechanical strength
- Inertness or chemical stability
- Low cost
- Good uniformity.

### 3.2.3 SUBSTRATE CLEANING

A clean and contaminant-free substrate is needed for durable and adherent coating. In the growth of films, cleanliness exerts a decisive influence. Thus a thoroughly cleaned substrate is a prime request for the preparation of films. Fingerprints, residues, oil and airborne particles are the usual contaminants. While cleaning, the contaminates are removed from the substrates. The procedure followed in the present study to clean the glass substrate is described below. Initially the glass substrate of dimension 75mm X 25mm with thickness of 1mm is cleaned with an acidic bath containing hydrochloric acid and nitric acid in the ratio 1:3 by immersing the substrate for an hour. Thereafter, substrate is rinsed with the deionised water. Then, the substrate cleaned with extran

solution. Finally the substrates are again rinsed with deionised water and are dried in desiccators [59].

### 3.2.4 SUCCESSIVE IONIC LAYER ADSORPTION AND REACTION METHOD

SILAR is a process for depositing uniform, crystalline and conformal thin films by alternating exposures to cation and anion. SILAR has been successfully demonstrated for many metals. SILAR is based on immersion of the substrate into separately placed cations and anions. Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution [60]. SILAR method is inexpensive, simple and convenient for large area deposition. Titanium tri chloride and Ammonium hydroxide were used as cationic and anionic sources respectively. Thus providing compact, uniform films with control over thickness of the film. The preparative conditions such as concentration of the precursor, nature of complexing agent, pH of the precursor solution and adsorption, reaction and rinsing time duration etc, are to be optimized to get good quality $TiO_2$ thin films (Fig 3.1) [23].

#### 3.2.4.1 ADVANTAGES OF SILAR

- SILAR does not require high quality target and/or substrates nor it does require vacuum at any stage
- The deposition rate and thickness of the film can be easily controlled over a wide range by changing the deposition cycles.
- It offers extremely easy way to dope films
- There are virtually no restrictions on substrate material, dimension or its surface profile; moreover it is convenient for large area deposition [60].

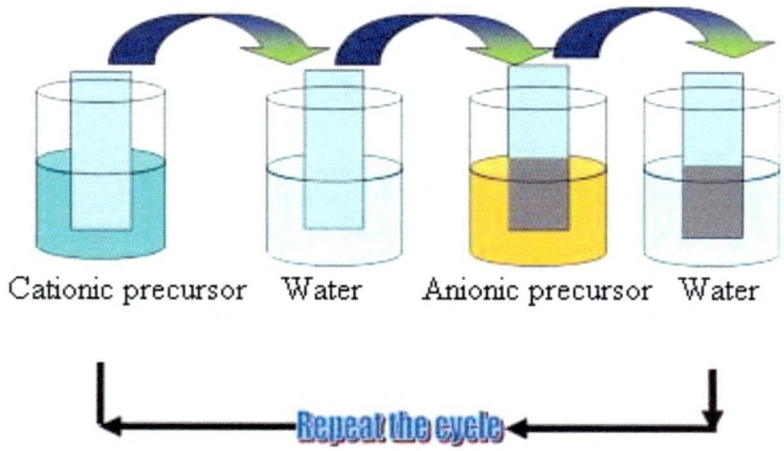



**Fig 3.1 Deposition of film by Successive Ionic Layer Adsorption and Reaction method**

### 3.2.5 PREPARATION OF $TiO_2$ THIN FILM

In the present work, $TiO_2$ films are deposited onto the glass substrate by SILAR technique. Titanium tri chloride and ammonium hydroxide are used as the cationic and anionic precursors respectively. Deionised water is used for rinsing the substrates between successive immersion in the cationic and anionic precursors. Suitable volumes of cationic and anionic precursor solutions are taken in beaker, in addition to, the deionized water. The solutions are stirred well to obtain homogeneous solution. Films are obtained by repeating the SILAR cycle for number of times. To study the effect of immersion time on the properties of the $TiO_2$ films, samples are deposited at different immersion times with constant precursor concentration and number of reaction cycles. In a typical deposition, the substrate was immersed in $TiCl_3$ for 20 seconds when the $Ti^+$ ions adsorbed to the substrate surface followed by a rinsing in deionised water for 5 sec.The substrate was then immersed in ammonium hydroxide solution for 40 sec and during this process $OH^-$ ions react with the $Ti^+$ ions preadsorbed on the substrate to form $TiO_2$ film. Finally the substrate was rinsed in deionised water for 5 sec to remove the loosely bound ions. The films were deposited by varying the adsorption/reaction time. Then, repeating the cycle for 100 times. Finally substrates were placed in desiccator for drying.

The procedure was repeated by varying the immersion time in the precursors and the film deposition conditions are depicted in table 3.1. The deposited films were annealed at 450°C for 5h. The annealed $TiO_2$ thin films are used for dye sensitization.

**Table 3.1 Film Deposition Condition**

| Samples | Concentration of precursor (Vol in %) | | Immersion time in Cation precursor (sec) | Immersion time in Anion precursor (sec) | Rinsing time (sec) | No of SILAR cycle (min) |
|---|---|---|---|---|---|---|
| | $TiCl_3$ | $NH_3OH$ | | | | |
| 1 | 0.5 | 5 | 20 | 20 | 5 | 100 |
| 2 | 0.5 | 5 | 40 | 20 | 5 | 100 |
| 3 | 0.5 | 5 | 20 | 40 | 5 | 100 |
| 4 | 0.5 | 5 | 30 | 60 | 5 | 100 |

## 3.3 EXTRACTION OF NATURAL DYE AND DYE SENSITATION

$TiO_2$ films deposited by SILAR method are sensitized by the natural dye obtained from *Eugenia Jambolana.* Initially, the *Eugenia Jambolana* fruits are collected, shade dried and powdered. Ethanol is used as the solvent for the extraction of natural dye. The film is dipped in the dye solution for 3hrs. The molecular structure of pigment present in *Eugenia Jambolana* is shown in Fig 3.2.

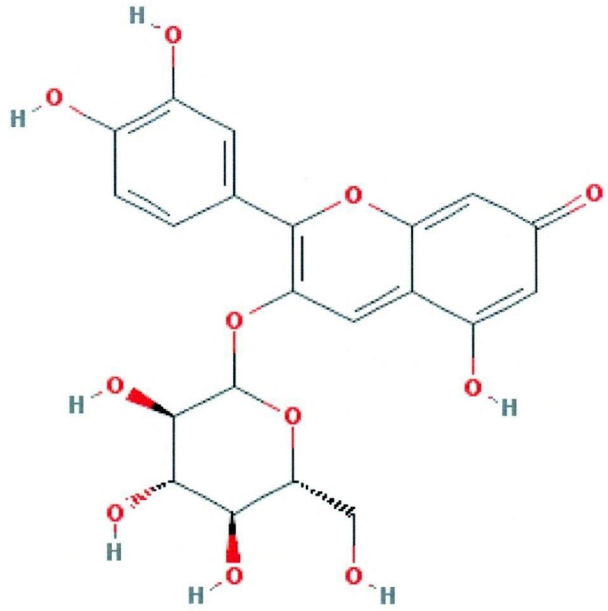


**Fig 3.2 Structure of cyanidin-3-O-glucoside**

### 3.4 THICKNESS MEASUREMENT

Different techniques have been developed for the measurement of thickness of the films. Thickness measurement technique may be broadly classified into the following categories such as electrical method, optical method, magnetic method, gravimetric method etc. In the present work, thickness is measured by gravimetric method.

### 3.4.1GRAVIMETRIC METHOD

In this technique, mass of the substrate is measured before and after deposition and the difference between the masses gives the mass of the material deposited. From which thickness is calculated using the formula,

$$t = m/a \times d$$

Where,

t=film thickness (m)

a =area of the sample in $cm^2$.

m=mass of the film (g)

d=density of the material in g/ ($cm^3$) [61].

## 3.5 OPTICAL CHARACTERIZATION

The knowledge of optical property of solid films has widely contributed to the phenomenal growth of their application. Optical characterization of films is strongly influenced by the process parameters and the deposition method. Thin films are primarily characterized by absorption/transmission and refractive index. The optical study of solid is concerned with the interaction of the photon energy with matter and the consequent changes occurring in the electronic status. From reflection, transmission and absorption process, the optical constants such as transmittance, absorption coefficient (α) and band gap are evaluated.

### 3.5.1 ULTRAVIOLET AND VISIBLE SPECTROSCOPY

Ultraviolet–visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges.The instrument used in ultraviolet-visible spectroscopy is called a UV/Vis spectrophotometer. It measures the intensity of light passing through a sample (I), and compares it to the intensity of light before it passes through the sample ($I_o$). The ratio $I / I_o$ is called the transmittance, and is usually expressed as a percentage (%T). The absorbance, A, is based on the transmittance:

$$A = -\log (T/100)$$

The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating in a monochromator or a prism to separate the different wavelengths of light, and a detector. A spectrophotometer can be either single beam or double beam. In a double-beam instrument, the light is split into two beams before it

reaches the sample. One beam is used as the reference; the other beam passes through the sample.

Components of a typical spectrometer are shown in the following diagram (Fig 3.3). The functioning of this instrument is relatively straightforward. A beam of light from a visible and/or UV light source is separated into its component wavelengths by a prism or diffraction grating. Each monochromatic (single wavelength) beam in turn is split into two equal intensity beams by a half-mirrored device. One beam, the sample beam, passes through a small transparent container (cuvette) containing a sample. The other beam, the reference, passes through an identical cuvette. The intensities of these light beams are then measured by electronic detectors and compared. The intensity of the reference beam, which should have suffered little or no light absorption, is defined as $I_0$. The intensity of the sample beam is defined as I. Over a short period of time, the spectrometer automatically scans all the component wavelengths in the manner described. The ultraviolet (UV) region scanned is normally from 200 to 400 nm, and the visible portion is from 400 to 800 nm [62].

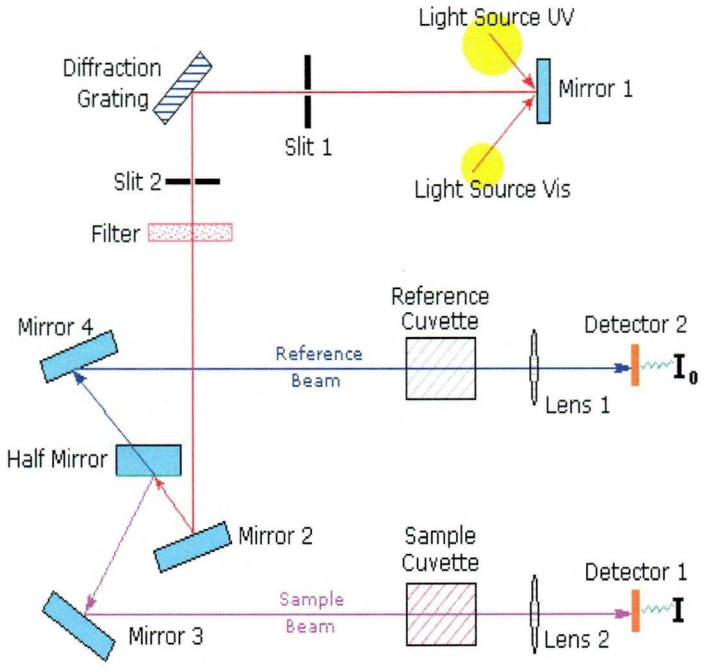



**Fig 3.3 UV-VIS spectrophotometer**

### 3.5.2 OPTICAL PARAMETERS

#### i) Extinction coefficient

The extinction coefficient (K) is calculated making use of Lambert's eqution,

$$I = I_0 \exp(4\pi kt/\lambda)$$

Where,

$\lambda$ = Wavelength of light

t = Thickness of the material

Thus the value of k can be determined from the formula,

$$k = \frac{2.303 \times \log(1/T) \times \lambda}{4\pi t}$$

#### ii) Absorption coefficient

The absorption coefficient is calculated using the relation,

$$\alpha = \frac{4\Pi k}{\lambda}$$

t=Thickness of the film,

#### iii) Band gap

In a material, the energy difference between its non-conductive state and its conductive state is called Band gap. There is virtually no band gap in most metals, but a very large one in an insulator (dielectric). In a semiconductor, the band gap is small. Technically, the band gap is the energy it takes to move electrons from the valence band to the conduction band. The energy band gap is determined using absorption spectra with

the help of Tauc relation. Using this relation, a graph is plotted between the square of ($\alpha h\nu$) and $h\nu$ to obtain a straight line. [63]

$$\alpha h\nu = A\,(h\nu - E_g)^{n}$$

**iv) Direct transition**

The band gap is called "direct" if the momentum of electrons and holes is the same in both the conduction band and the valence band; an electron can directly emit a photon [64].

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

## 3.6 STRUCTURAL CHARACTERIZATION

The microstructure of the film is found to have profound influence on the optical, electrical and mechanical film properties. X-ray diffraction technique plays a vital role in all aspects of semiconductor technology from fundamental research to manufacturing. X-ray diffraction technique is a very simple and non-destructive technique requiring only very small area of the sample. This method is used to find whether the given material is crystalline or amorphous. Hence the structural characterization of $TiO_2$ film (various compositions) has been carried out using X-ray diffractrometer (Fig3.4) and the various micro structural parameters have been estimated.

### 3.6.1 X-RAY DIFFRACTION (XRD)

Diffraction is one of the most powerful methods for the structural study of the materials, which may involve X rays, electron or neutrons. A zero phase shift between two or more waves reflected from the regular pattern of the studied sample gives the maximum intensity, while the wave in opposite phase will cancel each other and yield minimum intensity.

In the case of light reflected from a layered structure with the spacing (d) between the reflecting planes, the Bragg conditions for diffraction maxima can be obtained from the path difference ($n\lambda = 2d \sin \theta$) of the reflected rays from different crystal planes. The diffraction pattern reflects the distribution in reciprocal space of either the electron density in electron diffraction or atomic density in neutron diffraction. Therefore, the profile of electron or atomic density can be extracted from the respective diffraction pattern.

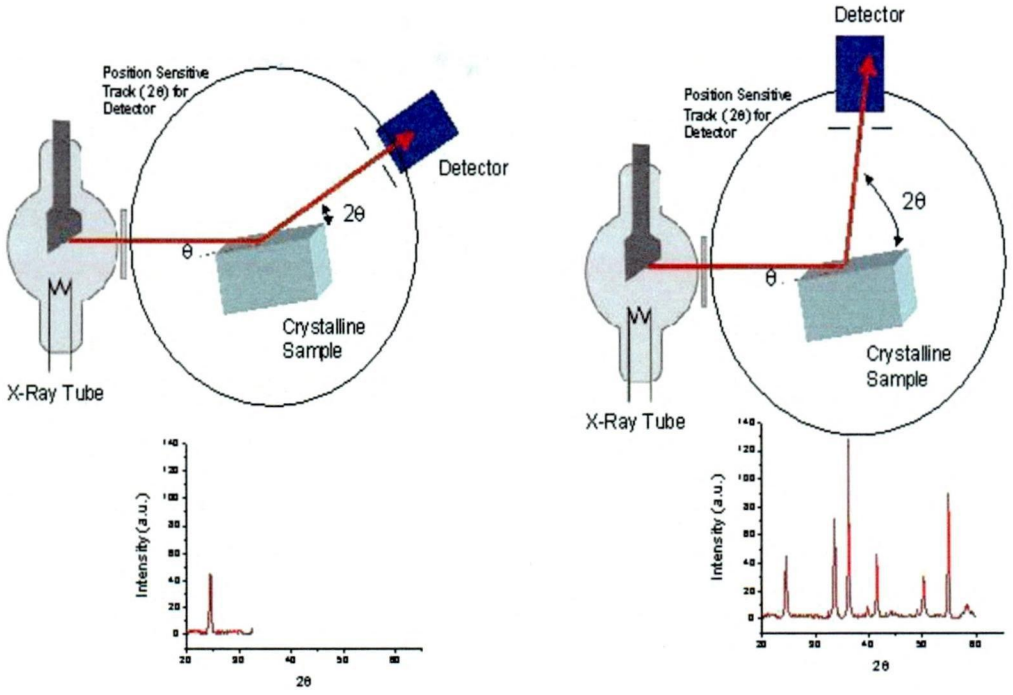



**Fig 3.4 X-ray Diffraction**

**i) THEORY**

If θ is the angle of incidence, then the path difference between two waves is "2d sinθ".By Braggs law,

$$\mathbf{2d \sin \theta = n\lambda}$$

Where,

n = Order of reflection.

d = Distance between the atomic planes parallel to the axis of incident beam.

$\lambda$ = Wavelength of X-rays. (Fig 3.4) [65, 66]

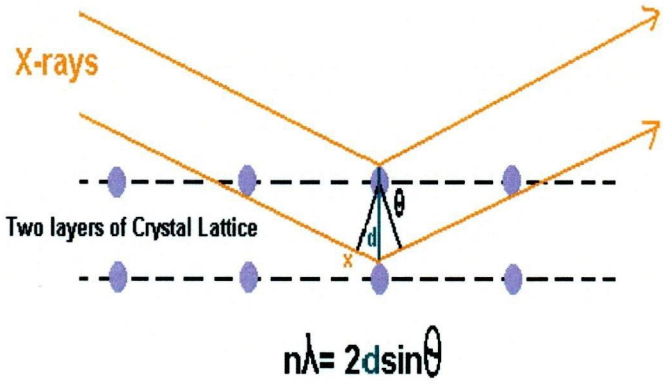



**Fig 3.5 Bragg's X-ray diffraction**

### 3.6.2 STRUCTURAL PARAMETERS

#### i) Grain size (D)

The grain size (D) has been calculated using the Scherrer's formula

$$D = k\lambda/\beta \cos\theta$$

Where,

K = slope factor 0.94,

$\lambda$ = Wavelength of x rays.

$\theta$ = Braggs angle,

$\beta$ = Full width half maximum in radian.

**ii) Interplanar spacing ($d_{hkl}$)**

From the XRD profiles, the interplanar spacing $d_{hkl}$ has been calculated using the Braggs relation.

$$d_{hkl} = n\lambda/2 \sin\theta$$

Where,

$\theta$ = Braggs angle,

n = Order of diffraction,

$\lambda$ = Wavelength of incident X-rays.

**iii) Lattice constant (a)**

The lattice constant refers to the constant distance between unit cells in a crystal lattice. Lattices in three dimensions generally have three lattice constants, referred to as *a*, *b*, and *c*.

$$a = d_{hkl}/\sqrt{h^2+k^2+l^2}$$

**iv) Micro strain ($\varepsilon$)**

The micro strain ($\varepsilon$) is obtained using the relation

$$\varepsilon = \beta \cos\theta/4$$

Where,

$\beta$ = Full width half maximum of the peak,

$\theta$ = Diffraction angle [67].

## 3.7 SURFACE CHARACTERIZATION

### 3.7.1 SCANNING ELECTRON MICROSCOPY (SEM)

The electron beam, which typically has an energy ranging from 0.2 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the $x$ and $y$ axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to around 5 μm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a computer monitor (or, for vintage models, on a cathode ray tube). Each pixel of computer videomemory is synchronised with the position of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. In older microscopes image may be captured by photography from a high-resolution cathode ray tube, but in modern machines image is saved to a computer data storage.

**Magnification:**

Magnification in a SEM can be controlled over a range of up to 6 orders of magnitude from about 10 to 500,000 times. Unlike optical and transmission electron

microscopes, image magnification in the SEM is not a function of the power of the objective lens. SEMs may have condenser and objective lenses, but their function is to focus the beam to a spot, and not to image the specimen. Provided the electron gun can generate a beam with sufficiently small diameter, a SEM could in principle work entirely without condenser or objective lenses, although it might not be very versatile or achieve very high resolution. In a SEM, as in scanning probe microscopy, magnification results from the ratio of the dimensions of the raster on the specimen and the raster on the display device. Assuming that the display screen has a fixed size, higher magnification results from reducing the size of the raster on the specimen, and vice versa. Magnification is therefore controlled by the current supplied to the x, y scanning coils, or the voltage supplied to the x, y deflector plates, and not by objective lens power[68,69][Fig 3.6].

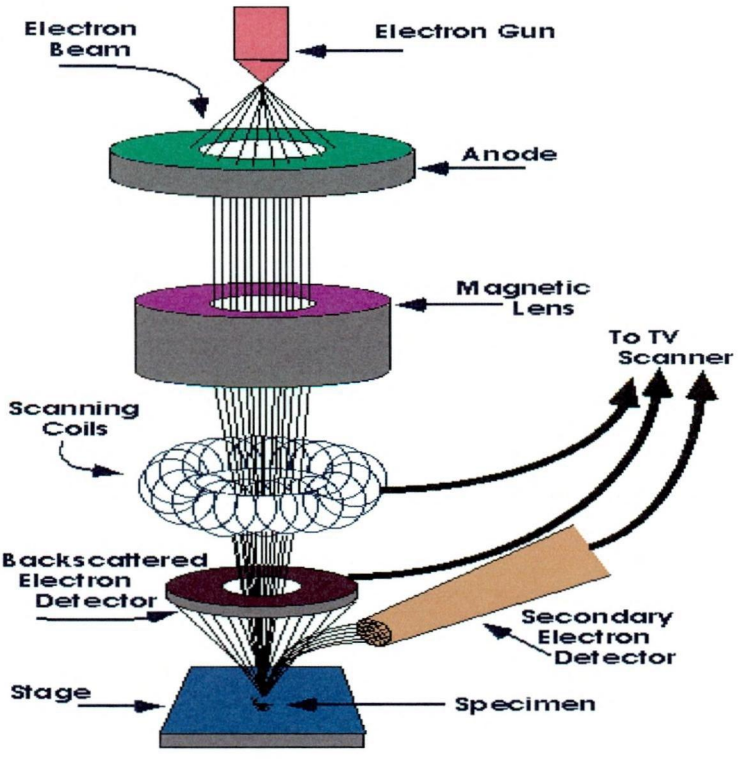



**Fig 3.6 Schematic diagram of Scanning Electron Microscopy**

## 3.8 ENERGY DISPERSIVE X-RAY ANALYSIS (EDAX)

EDX Analysis stands for Energy Dispersive X-ray analysis. It is sometimes referred to also as EDS or EDAX analysis. It is a technique used for identifying the elemental composition of the specimen, or an area of interest thereof. The EDX analysis system works as an integrated feature of a scanning electron microscope (SEM), and cannot operate on its own. During EDX Analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms' own electrons, knocking some of them off in the process. A higher-energy electron from an outer shell eventually occupies a position vacated by an ejected inner shell electron. However, the transferring outer electron must give up some of its energy by emitting an X-ray. The amount of energy released by the transferring electron depends on which shell it is transferring from, as well as which shell it is transferring to. Furthermore, the atom of every element releases X-rays with unique amounts of energy during the transferring process. Thus, by measuring the amounts of energy present in the X-rays being released by a specimen during electron beam bombardment, the identity of the atom from which the X-ray was emitted can be established. An EDX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well. For example, a peak corresponding to the amount of energy possessed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a K-Alpha peak. The peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a K-Beta peak (Figure 3.9) [70].

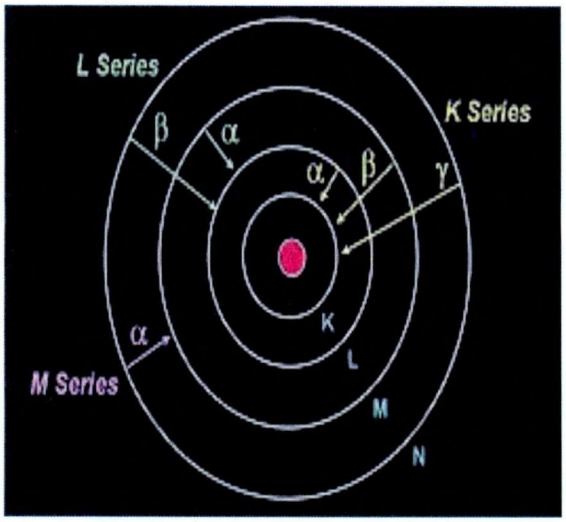



**Figure 3.7 Elements in an EDAX spectrum**

## 3.9 PHOTOLUMINSCENCE SPECTROSCOPY (PL)

Photoluminescence spectroscopy is a contact less, nondestructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation [Fig 3.7] One way this excess energy can be dissipated by the sample is through the emission of light, or luminescence. In the case of photo-excitation, this luminescence is called photoluminescence. The intensity and spectral content of this photoluminescence is a direct measure of various important material properties.Photo-excitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and may include the emission of light (a radiative process) or may not (a nonradiative process). The energy of the emitted light (photoluminescence) relates to the difference in energy levels between the two electron states involved in the transition between the excited state and the equilibrium state. The quantity of the emitted light is related to the relative contribution of the radiative process. The measurement of photoluminescence from semi-conductor materials has become an important characterisation method and is widely accepted to provide information on for example: carrier doping levels, alloy

compositions, film structures, band gap and edge effects, etc. in applications ranging from scientific research, process monitoring, or device characterisation.

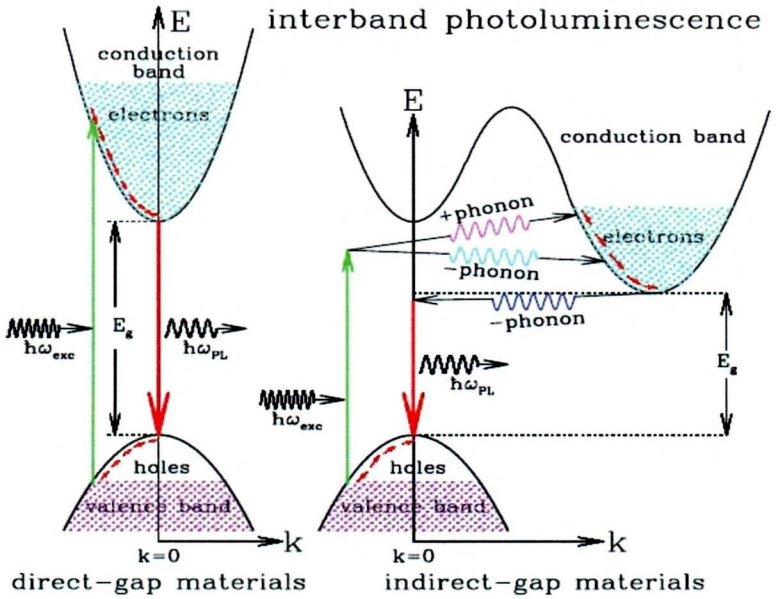



**Fig 3.8 Schematic band diagrams for the photoluminescence processes**

**i) Band Gap Determination:** The most common radiative transition in semiconductors is between states in the conduction and valence bands, with the energy difference being known as the band gap. Band gap determination is particularly useful when working with new compound semiconductors.

**ii) Impurity Levels and Defect Detection:** Radiative transitions in semiconductors also involve localized defect levels. The photoluminescence energy associated with these levels can be used to identify specific defects, and the amount of photoluminescence can be used to determine their concentration.

**iii) Recombination Mechanisms**: The return to equilibrium, also known as "recombination," can involve both radiative and nonradiative processes. The amount of photoluminescence and its dependence on the level of photo-excitation and temperature are directly related to the dominant recombination process. Analysis of

photoluminescence helps to understand the underlying physics of the recombination mechanism.

**iv) Material Quality:** In general, nonradiative processes are associated with localized defect levels, whose presence is detrimental to material quality and subsequent device performance. Thus, material quality can be measured by quantifying the amount of radiative recombination [71].

## 3.10 FOURIER TRANSFORM INFRARED SPECTROSCOPY(FTIR)

In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis.

FTIR is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantities some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. Today's FTIR instruments are computerized which makes them faster and more sensitive than the older dispersive instruments. [72] In Fourier Transform Infrared Spectroscopy (FTIR), a spectrum showing molecular vibrations is obtained, in order to identify or characterize organic materials such as polymers, lubricants, adhesives and cleaning agents. A limited number of inorganic compounds can also be evaluated using FTIR. For semiconductors, FTIR is used to make quantitative measurements of hydrogen bonds in silicon nitride films and to measure the interstitial oxygen content in bulk silicon. FTIR is an effective analytical tool for identification of unknowns, sample screening and profiling samples Fig 3.8 [73].

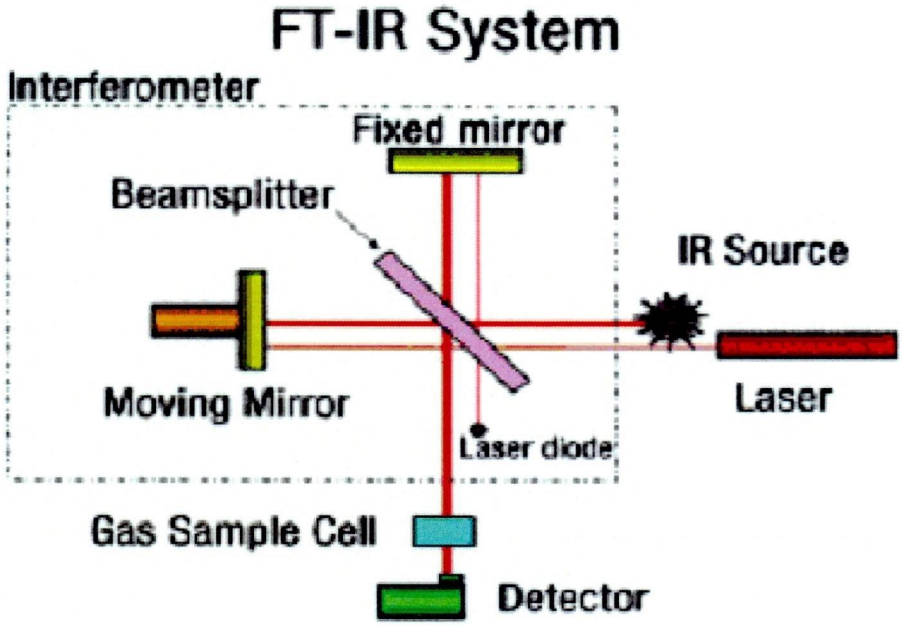


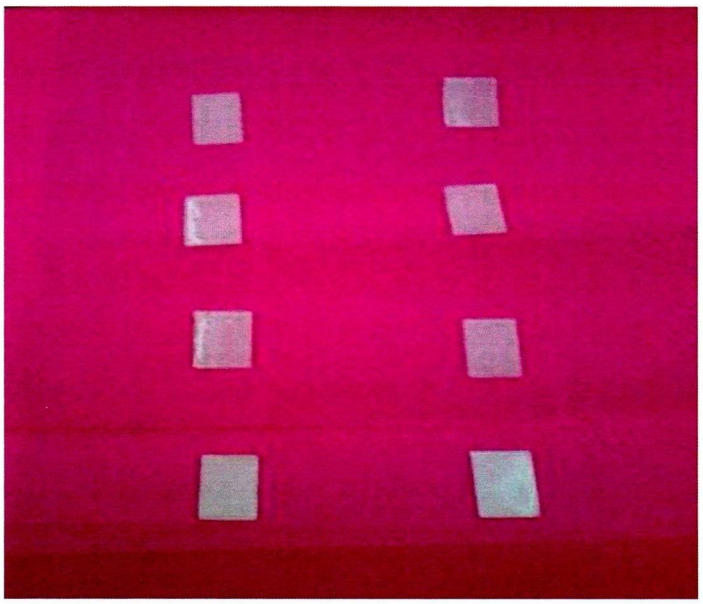

**Fig 3.9 Schematic diagram of Fourier Transforms Infrared Spectrometer**

**Plates 3.1**

**Set up for $TiO_2$ thin films deposition by SILAR method**

**Plates 3.2**

**As-Deposited $TiO_2$ thin films**

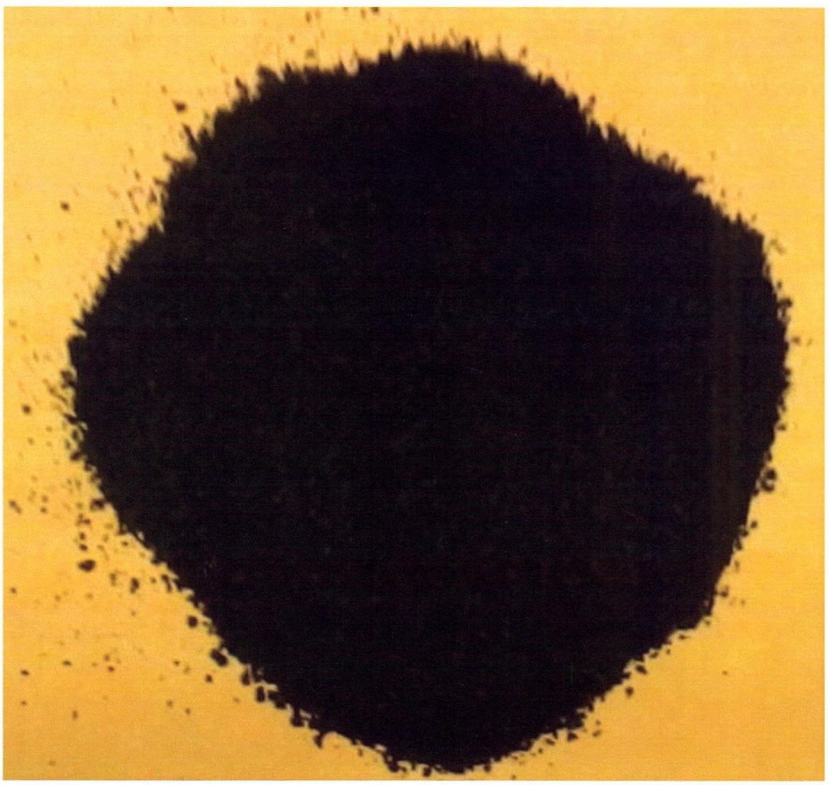


**Plates 3.3**

**Fruits of *Eugenia Jambolana***

**Plates 3.4**

***Eugenia Jambolana* powder**



**Plates 3.5**

**Dye extracted from *Eugenia Jambolana***

**Plates 3.6**

**Dye sensitized$TiO_2$ thin films**