CHAPTER – 2

THEORETICAL BACKGROUND AND EXPERIMENTAL TECHNIQUES
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In this chapter we discuss briefly the growth of semiconductor nanocrystals (quantum dots) in glass matrix. The famous Lifshitz and Slezov model 1961 [1] for condensation from supersaturated solid solution is often used to describe the growth process of semiconductor quantum dots in glasses and is therefore presented here. A concise discussion of the major characterization techniques used in the present study i.e. X-ray diffraction (XRD), Thermal Analysis (DTA, DSC), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Spectroscopy (EDAX), UV-Vis Spectroscopy, Photoluminescence (PL), Raman Spectroscopy is also described.

2.1 Diffusion controlled growth process

To understand all basic properties of three-dimensional confinement in semiconductor doped glasses, understanding of the growth process is an indispensable requirement. We start the attempts to find a functional description of the growth process, or generally of phase transitions from a conventional homogeneous nucleation theory given by R. Becker and D. Siring 1935 [2]. At constant temperature the phase transition proceeds between a supersaturated vapor of $m$ monomers (molecules) and droplets containing $im$ ($i > 2$) monomers. The rate equation (Equation. 2.1) determines the number of monomers $m$ inside the droplets (clusters) and relates the gain $G_m$ and the losses $L_m$, where the size of the clusters changes by the gain or the loss of one monomer

$$\frac{dm}{dt} = G_m - L_m$$

(2.1)
The resulting change in the monomer density \( \frac{dm}{dt} \) is determined by the difference between the number of monomers impinging on and evaporating from the cluster through the surface into the supersaturated vapor phase. The growth mechanism is expressed by introducing the explicit terms for \( G \) and \( L \). The primary aim of growth analysis is to estimate asymptotic functions for the cluster size distribution. Involving detailed expressions for \( G \) and \( L \) in Equation (2.1) and combining this equation with the matter conservation law and the equation of continuity, the cluster growth laws have been calculated.

**Lifshitz-Slezov Model**

In this model an analysis is made of the process whereby diffusion effects can cause the precipitation of grains of a second order phase in a supersaturated solid solution.

Let \( C_\infty \) be the concentration of the saturated solution then a parameter ‘\( \alpha \)’ is defined as

\[
\alpha = \frac{2\sigma}{kT} \sqrt{C_\infty}
\]  

where \( \sigma \) is the inter–phase surface tension, \( v \) is the atomic volume of the solute. If \( R \) is the grain radius and \( C_R \) is the equilibrium concentration at the boundary of a grain then

\[
C_R = C_\infty + \frac{\alpha}{R}
\]  

The degree of supersaturation is small so that \( C - C_\infty = \Delta \ll 1 \). The mean distance between grains is much higher than their dimension therefore for present case we may ignore the interaction between grains. In Lifshitz-Slezov model it is assumed that the transport of monomers to the cluster surface is realized by diffusion in a supersaturated solution. Then the diffusion current of solute across the grain is given as

\[
j = \frac{dR}{dt} = D \frac{\partial c}{\partial r} = \frac{D}{R} \left( C - C_R \right)
\]  

\[
\frac{dR}{dt} = \frac{D}{R} \left( \Delta - \frac{\alpha}{R} \right)
\]

where \( D \) is the diffusion coefficient and \( \Delta \) is the supersaturation. From Equation (2.4) one can say that supersaturation is a function of time. Thus, for every value of \( \Delta \) of the supersaturation there is a critical radius \( R_c = R_c(t) \), for which the grain is in equilibrium with the solute. The initial critical radius is
If \( R > R_c(t) \) the grain will grow.

If \( R < R_c(t) \) the grain will dissolve.

Now we introduce an expression for size distribution function \( f(R, t) \), for clusters with radius \( R \) at the time \( t \). The continuity equation of the probability density in cluster space coordinates is

\[
\frac{\partial f(R^3, t)}{\partial t} + \frac{\partial [f(R^3, t) \cdot \hat{R}]}{\partial R^3} = 0
\]

(2.6)

\( \hat{R} = dR/dt \) is the cluster growth velocity and can be determined from the rate Equation (2.1). This can be done by the transformation of the average number of monomers per cluster to the average cluster size \( \langle R \rangle \) and the consideration of the conservation of the total amount of matter. The solution of Equation (2.6), and thus \( f(R^3, t) \), depends on the different mechanisms considered for \( G_m \) and \( L_m \) and leads to different expressions for \( \hat{R} \) [3].
Figure 2.1: Concentration profile around the nanocluster during the growth process. $\bar{C}$ is the average concentration within the supersaturated solution and $C_o$ is the concentration inside the nanocluster.

Figure 2.1 shows the growth process of a supersaturated solution. A small cluster is unstable because the concentration around it is too high, and a large cluster is instable because there is a very low concentration and presence of depletion region around it. The monomers feel a concentration gradient driving the diffusion of matter from smaller to larger clusters. A diffusion-controlled competitive growth of the nanoclusters is the result. In the framework of the Lifshitz-Slezov analysis, the asymptotically stable size is the one for which the concentration directly near the surface $C_R$ is equal to the average concentration of the matrix ($C_R = \bar{C}$).

Using the Lifshitz-Slezov model to the growth process in glass matrix, the surface free energy, one of the parameters determining $R_c$, will depend on both matrix environment and semiconductor material. Furthermore, in the Lifshitz-Slezov analysis the number of nuclei is considered to be constant. To avoid a high formation rate of nuclei, a low value of supersaturation is required. When we carry out the asymptotic analysis we find that the final size distribution evaluated by Lifshitz and Slezov is asymmetrical and independent of the initial distribution [4]. Its maximum value does not correspond to the critical radius and is slightly shifted to larger radii $R > R_c$. The slope to larger sizes is abrupt and nanoclusters of sizes larger than twice the critical radius do not exist. However, the function gradually decreases toward smaller sizes with a long tail.

The volume of the cluster grows linearly in time corresponding to the following equation

$$R_{average} = \left[\frac{4aDt}{9}\right]^{1/3} \quad (2.7)$$

2.2 Synthesis of semiconductor doped glass

To fabricate semiconductor nanocrystals in glass the conventional quench method was adopted [4, 5]. Over twenty different glass compositions were optimized to get suitable
host glass batch composition that is compatible for the nucleation and growth process of semiconductor (CdS, CdSe and Sb₂S₃ semiconductors for present study) nanocrystals quantum dots. Table 2.1 shows some selective glass batch compositions. In each composition glass constituent oxides were taken in the weight percentage of the total glass composition.

**Table 2.1:** Different glass compositions used for growth of semiconductor quantum dot.

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiO₂ Wt.%</th>
<th>B₂O₃ Wt.%</th>
<th>Na₂O Wt.%</th>
<th>CaO Wt.%</th>
<th>K₂O Wt.%</th>
<th>ZnO Wt.%</th>
<th>TiO₂ Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass Composition 1</td>
<td>55</td>
<td>8</td>
<td>5</td>
<td>-</td>
<td>25</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Glass Composition 2</td>
<td>60</td>
<td>5</td>
<td>25</td>
<td>5</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Glass Composition 3</td>
<td>60</td>
<td>20</td>
<td>9.6</td>
<td>6</td>
<td>4</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>Glass Composition 4</td>
<td>55</td>
<td>20</td>
<td>20</td>
<td>-</td>
<td>1</td>
<td>4</td>
<td>-</td>
</tr>
</tbody>
</table>

Here, we are briefly presenting the experimental work. The detailed information about specific experimental procedure and numeric data such as melting temperature, annealing temperature etc. for each semiconductor (CdS, CdSe and Sb₂S₃) is given in the concerned chapter. The general synthesis procedure is as follows:

- The glass constituent compounds were weighed according to their weight percentage shown in Table 2.1. An electronic balance (Shimadzu, AUW 120D) shown in Figure 2.2, with single pan and accuracy up to five decimal places is used in this study.

- To ensure proper mixing and homogeneity of the composition, the base glass constituents were mixed by wet ball milling using tungsten / zirconia (ZnO₂) balls and double distilled water. Liquid media is used to facilitate uniform mixing. Duration of milling generally depends on requirement. Usually, 12-24 hrs milling is sufficient for uniform mixing of starting powders. Weight of balls and that of powders are kept at 5:1 ratio. This wet mixture was dried in electric oven at 90 °C.
for 10 - 20 hrs. Figure 2.3 shows the ball milling machine and zirconia balls used in this study.

Figure 2.2: Electronic balance used to weigh chemical compounds.

- After drying, the composition was divided in two equal parts. One for reference glass and the other for semiconductor doped glass.
- 10 to 15 weight percent semiconductor was mixed in glass composition by again using wet ball milling.
- The glass compositions were melted in an alumina crucible at high temperature range 1100 °C to 1400 °C using high temperature box furnace shown in Figure 2.4 (a).
- The molten glass was quenched in different medium such as air/ liquid Nitrogen/ ice/ ice water.
- Glasses were then cut to prepare nearly 5mm x5mm dimension samples for further characterization.
- Platinum foil was used as a pan for thermal treatment of glass samples.
To find out the heat treatment range, glass transition temperature $T_g$ and crystallization temperature $T_{cry}$ thermal analyses were done using DSC measurements.

**Figure 2.3:** (a) The ball milling machine and (b) Zirconium balls and bottle that were used for mixing.

**Figure 2.4:** (a) High temperature box furnace used for glass melting and (b) Programmable furnace used for annealing process.
The dot sizes and their distributions were modified by annealing the glass samples at different temperatures between $T_g$ and $T_{melt}$. The heat treatment for various durations was carried out for glass samples at different temperature. Thus generated semiconductor doped glass (SDG) samples were characterized by X-ray diffraction (Rigaku MiniflexII), Differential Thermal Analysis (DTA) (Mettler Toledo TGA/DSC1 Star® System), Optical absorption (Hitachi U-3900H/Ocean Optics HR-4000), Photoluminescence (PL) (Horiba jobin yvon Fluorolog-3), Transmission Electron Microscopy (TEM) (FEI Technai G²T30), Scanning electron Microscopy (SEM) (Zeiss MA15) and Raman spectroscopy (Renishaw InVia Reflex Micro Raman Spectrometer).

2.3 Characterization Techniques

2.3.1 X-ray Diffraction

X-ray diffraction (XRD) is an excellent nondestructive powerful technique which is most widely used for uniquely identifying the crystalline phases present in the materials and general structural characterizations i.e. unit cell parameters, strain state, grain size, phase composition, preferred orientation, and defect structure, etc. It is inexpensive and easy to implement. A huge data bank (International Centre for Diffraction Data- ICDD) is available covering practically every possible phase of every known material, so it is routinely possible to determine phases in polycrystalline bulk material and to identify their relative amounts from diffraction peak intensities [6].

Beside phase identification, XRD is also used for particle size determination, measurement of thickness of thin films and multi-layers. The intensities measured with XRD data can provide quantitative accurate information on the atomic arrangements in amorphous materials including glass and polymers [6].
**Principle of X-Ray Diffraction**

The formulation of X-ray diffraction was first proposed by William Lawrence Bragg and William Henry Bragg in 1913 in response to their discovery that crystalline solids produced surprising patterns of reflected X-rays. They found that in these crystals, for certain specific wavelengths and incident angles, intense peaks of reflected radiation (known as Bragg peaks) were produced. The concept of Bragg diffraction applies equally to neutron diffraction and electron diffraction processes [7].

![Schematic representation of X-ray diffraction from crystal planes.](image)

**Figure 2.5**: Schematic representation of X-ray diffraction from crystal planes.

Principal of X-ray diffraction is illustrated in Figure 2.5. Since a beam of X-rays consists of a bundle of separate waves, the waves can interact with one another. If all the waves in the bundle are in same phase and there is no path difference (or constant path difference) between them then constructive interference will occur (path difference = nλ, where ‘n’ is an integer number). The waves will interfere and their amplitudes will add together to produce a resultant wave that has a higher amplitude.

If the waves are not in same phase, then destructive interference will occur and the amplitude of the waves will be reduced (path difference = 2n ± λ/2, where ‘n’ is an integer number).
Let us imagine a monochromatic X-rays beam is incident on a crystal with an angle $\theta$. In Figure 2.5 two X-rays are shown, where the spacing between the atomic planes is $d$. Ray 1 reflects from the upper atomic plane at an angle $\theta$ equal to its angle of incidence. Similarly, Ray 2 reflects from the lower atomic plane at the same angle $\theta$. While Ray 2 is in the crystal, it travels a extra distance of $2a$ extra than Ray 1. This is the effective path difference between two rays. Now from the condition for constructive interference:

$$\text{Path difference} = 2a = n\lambda$$

Now from figure we can work out the distance $2a$ in terms of the spacing ‘$d$ ’ between the atomic planes.

$$a = d \sin \theta \text{ or } 2a = 2d \sin \theta$$

Thus,

$$2d \sin \theta = n\lambda \quad (2.8)$$

This is known as Bragg's Law for X-ray diffraction.

If we know the wavelength, $\lambda$, of the X-rays and measure the angle $\theta$ of the diffracted X-rays coming out of the crystal, then one can get the spacing (referred to as d-spacing) between the atomic planes [8]. Again it is important to point out that this diffraction will only occur if the rays are in phase when they emerge, and this will only occur at the appropriate value of $n$ (1, 2, 3...) and $\theta$.

**X-ray Diffractometer**

In X-Ray Diffractometer (XRD) the Bragg-Brentano geometry shown in Figure 2.6 is used extensively for preferentially and randomly oriented powder or films [7-10]. The source (or focal point of incident beam), sample and receiving slit lie on the “focusing circle”, which has a radius dependent on $\theta$. In this geometry, slits collimate the incident X-rays that impinge the specimen at an angle $\theta$ which is not the angle between the incident beam and the specimen surface; rather it is the angle between the incident beam and the crystallographic plane that generate diffraction. After passing through receiving slits, the
diffracted X-rays are passed through a monochromator, then detected. In the Bragg-Brentano arrangement, the incident X-ray beam is fixed, the specimen is rotated at one half the angular velocity of the detector. During the scan, the angle between the sample surface and the incident beam changes, that is, illuminated area of the sample changes. Since the incident and diffracted X-rays make the same angle to the specimen surface, structural information is obtained only about (h k l) planes parallel to this surface.

![Bragg-Brentano focusing configuration](image)

**Figure 2.6:** Geometric arrangement of X-ray Diffractometer.

**Crystallite Size Measurement**

Phase identification using X-Ray diffraction depends on the positions of the peaks in a diffraction profile as well as the relative intensities of these peaks to some extent. Another aspect of the diffraction from material is the importance to consider how diffraction peaks are changed by the presence of various types of defects such as small number of dislocations in crystals with dimensions of millimeters [9]. Small size of grain size can be considered as another kind of defect and can change diffraction peak widths. Very small crystals cause peak broadening. The crystallite size is easily calculated as a function of peak width (specified as the full-width at half maximum (FWHM) peak intensity), peak position and wavelength.
Particle Size Determination (Scherrer’s Formula)

Suppose that the crystal has a thickness $\delta$ measured in a direction perpendicular to a particular set of Bragg planes (Figure 2.7(a)). Let there be $(m + 1)$ planes in this set. Define the Bragg angle as a variable and let $\theta_B$ be the angle which exactly satisfies Bragg’s law for the particular values of $\lambda$ and $d$ involved, then

$$\lambda = 2d \sin \theta_B$$

In the Figure 2.7(a), rays A, D… M make exactly this angle $\theta_B$ with the diffraction planes. Incident X-rays that make angles only slightly different from $\theta_B$ produce incomplete destructive interference. Ray B, for example, makes a slightly larger angle $\theta_1$, such that ray $L'$ from the $m^{th}$ plane below the surface is $(m + 1)$ wavelengths out of phase with $B'$, the ray from the surface plane. The intensity of the beam diffracted at an angle $2\theta_1$ is therefore zero. It is also zero at an angle $2\theta_2$, where $\theta_2$ is such that ray $N'$ from the $m^{th}$ plane below the surface is $(m -1)$ wavelengths out of phase with ray $C'$ from the surface plane. This defines, therefore, the two limiting angles, $2\theta_1$ and $2\theta_2$, at which the diffracted intensity must drop zero.

![Figure 2.7: Effect of crystallite size on diffraction pattern.](image-url)
The curve of diffracted intensity vs. $2\theta$ will thus have the form of Figure 2.7 (b) in contrast to Figure 2.7 (c), which illustrates the hypothetical case of diffraction occurring only at the exact Bragg angle. The width of the diffraction curve of Figure 2.7 (b) increases as the thickness of crystal decreases, because the angular range $(2\theta_1 - 2\theta_2)$ increases as $m$ decreases. The width $B$ is usually measured, in radians, at an intensity equal to half the maximum intensity (FWHM).

Therefore,

$$B = \frac{1}{2} (2\theta_1 - 2\theta_2)$$

(2.9)

The path-difference equations for these two angles are similar, but related to the entire thickness of the crystal rather than to the distance between adjacent planes:

$$2\delta \sin \theta_1 = (m+1)\lambda$$

$$2\delta \sin \theta_2 = (m-1)\lambda$$

By subtraction,

$$\delta (\sin \theta_1 - \sin \theta_2) = \lambda$$

$$2\delta \cos \frac{(\theta_1 + \theta_2)}{2} \sin \frac{(\theta_1 + \theta_2)}{2} = \lambda$$

But $\theta_1$ and $\theta_2$ are both very nearly equal to $\theta_B$, so that

$$\theta_1 + \theta_2 = 2\theta_B$$

$$\sin \frac{(\theta_1 - \theta_2)}{2} = \frac{(\theta_1 - \theta_2)}{2}$$

Therefore,

$$2\delta \frac{(\theta_1 - \theta_2)}{2} \cos \theta_B = \lambda$$

or

$$\delta = \frac{\lambda}{B \cos \theta_B}$$
More exactly,

\[
\delta = \frac{0.9 \lambda}{B \cos \theta_B}
\]

(2.10)

This is known as Scherrer’s formula. It is used to estimate the crystallite size from measured width of their diffraction curves. Note that whether a value of 0.9 or 1 is used depends on shapes of the crystallites assumed to be sample [10].

In the present work X-ray diffraction patterns have been observed for semiconductor doped glass and undoped glass matrices. From the XRD pattern, following information can be obtained: (i) Amorphous nature of reference glass samples, (ii) Phase confirmation of the semiconductor quantum dots, (iii) The unit cell dimension and lattice type and (iv) Particle size of nanocrystals.

![Figure 2.8: Photograph of X-ray diffraction system used in this study (Rigaku Miniflex II).](image)

In the present study, X-ray diffraction patterns at room temperature were recorded using Rigaku Miniflex II with CuKα₁ (\(\lambda=1.5418 \, \text{Å} \)) shown in Figure 2.8. The \(2\theta\) range was 10°
to 80° with step size of 0.02° and scan speed from 0.5° to 4° per minute. The obtained XRD patterns were analyzed by Powder X software.

### 2.3.2 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) has become a mainstay in the repertoire of material characterization techniques. It is an established technique for examining the crystal structure and the microstructure of materials such as metals, ceramics, semiconductors, polymers, and composites, etc. [6]. TEM’s strong cards are its high lateral spatial resolution (better than 0.2 nm “point-to-point” on some instruments) and its capability to provide both image and diffraction information from a single sample. With the common availability of high-voltage TEM instruments today, a growing emphasis is being placed on atomic resolution imaging. Future trends include the use of ultrahigh vacuum TEM instruments for surface studies and computerized data acquisition for quantitative image analysis. In 1938 the first commercial TEM instrument was produced by Siemens-Halske Company in Berlin [11].

#### Basic Principle

Transmission electron microscopy is similar to optical microscopy, except that the photons are replaced by electrons. Since electrons have a much smaller wavelength than photons, the diffraction barrier is less of an issue and much higher resolution can be achieved. The shorter wavelength of electrons (200 keV electrons have a wavelength of 0.025 Å) makes it possible to get a high-resolution (0.2 nm). TEM has high-magnification thousands times better than the light microscope. In TEM, a focused electron beam is incident on a thin (less than 200 nm) sample. The signal in TEM is obtained from both undeflected and deflected electrons that penetrate the sample thickness. A series of magnetic lenses at and below the sample position are responsible for delivering the signal to a detector, usually a fluorescent screen, a film plate, or a video camera. Accompanying this signal transmission is a magnification of the spatial information in the signal by as little as 50 times to as much as a factor of $10^6$. This
remarkable magnification range is facilitated by the small wavelength of the incident electrons, and is the key to the unique capabilities associated with TEM analysis [12]. A schematic of a TEM instrument, showing the location of a thin sample and the principal lenses within a TEM column, is illustrated in Figure 2.9, which contains four parts: electron source, electromagnetic lens system, sample holder and imaging system. By propelling electrons at a thin sample, and detecting those transmitted through it, one is able to obtain a map of the local densities of the sample, as well as diffraction information when there are ordered structures such as crystals involved.

Figure 2.9: (a) The schematic outline of a TEM and (b) TEM instrument used in this work (FEI Technai G²T30).

- **Electron source:** The electron source consists of a cathode and an anode. The cathode is a tungsten filament which emits electrons when heated. A negative cap
confines the electrons into a loosely focused beam (Figure 2.10). The beam is then accelerated towards the specimen by the positive anode. Electrons at the rim of the beam will fall onto the anode while the others at the center will pass through the small hole of the anode. The electron source works like a cathode ray tube.

![Electron source of a TEM and imaging system.](image)

**Figure 2.10:** Electron source of a TEM and imaging system.

- **Electromagnetic lens system:** After leaving the electron source, the electron beam is highly focused using electromagnetic lens and metal apertures. The system only allows electrons within a small energy range to pass through, so that electrons in the electron beam will have a well-defined energy.

- **Sample holder:** The sample holder is a platform equipped with a mechanical arm for holding the specimen and controlling its position.

- **Imaging system:** The imaging system consists of another electromagnetic lens system and a screen shown in Figure 2.10. The electromagnetic lens system contains two lens systems, one for refocusing the electrons after they pass through the specimen, and the other for enlarging the image and projecting it onto the
screen. The screen has a phosphorescent plate which glows when being hit by electrons. Image forms in a way similar to photography.

TEM offers two modes of specimen observation, image mode and diffraction mode.

**1. Image Mode:** The image mode produces an image of the illuminated sample area. The image can contain contrast brought about by several mechanisms: mass contrast, due to spatial separations between distinct atomic constituents; thickness contrast, due to nonuniformity in sample thickness; diffraction contrast, which in the case of crystalline materials results from scattering of the incident electron wave by structural defects; and phase contrast. By using electrons accelerated to high voltages, atomic planes of the crystal can be resolved. In this mode, intermediate aperture is removed and only objective aperture is used. Intermediate lens is used to focus on the image plane of the objective lens. In image mode, two imaging systems are used:

(a) **Bright field image mode:** When an incident electron beam strikes a sample, some of the electrons pass directly through, while others may undergo slight inelastic scattering from the transmitted beam. Contrast in an image appears by differences in scattering. By inserting an aperture in the back focal plane, an image can be produced with these transmitted electrons. The resulting image is known as a bright field image. Bright field images are commonly used to examine micro-structural related features.

(b) **Dark field image mode:** If a sample is crystalline, many of the electrons will undergo elastic scattering from the various planes. This scattering produces many diffracted beams. If any one of these diffracted beams is allowed to pass through the objective aperture, an image can be obtained. This image is known as a dark field image. Dark field images are particularly useful in examining microstructural detail in a single crystalline phase.

**2. Diffraction mode:** The diffraction pattern that is always present in the back focal plane of the objective is brought into focus by the objective lens. Individual spots are seen when the specimen is a single crystal, while for polycrystalline material concentric
rings are observed. In diffraction mode, an electron diffraction pattern is obtained on the fluorescent screen, originating from the sample area illuminated by the electron beam. The diffraction pattern is entirely equivalent to an X-ray diffraction pattern: a single crystal will produce a spot pattern on the screen, a polycrystal will produce a powder or ring pattern (assuming the illuminated area includes a sufficient quantity of crystallites), and a glassy or amorphous material will produce a series of diffuse halos.

Interplanar distance, $d$ can be calculated from the expression:

$$ R.d = L.\lambda $$

where, $\lambda$ is the wavelength of the electron beam (0.025 Å for 200 kV), $R$ is the distance of a particular spot form the central bright spot and $L$ is the distance between the specimen and the diffraction plane, known as the lens constant or camera length.

**Electron Optics**

It is easiest to discuss the electron optics of a TEM instrument by addressing the instrument from top to bottom. Refer again to the schematic in Figure 2.9. At the top of the TEM column is an electron source or gun. An electrostatic lens is used to accelerate electrons emitted by the filament to a high potential (typically 100-1000 kV) and to focus the electrons to a cross-over just above the anode (the diameter of the cross-over image can vary from 0.5 to 30 µm, depending on the type of gun) [13]. The electrons at the cross-over image of the filament are delivered to the specimen by the next set of lenses on the column, the condensers. Most modern TEMs use a two-stage condenser lens system that makes it possible to

I. Produce a highly de-magnified image of cross-over at the specimen, such that only a very small sample region is illuminated (typically less than µm).

II. Focus the beam at “infinity” to produce nearly parallel illumination at the specimen.

The former procedure is the method of choice during operation in the image mode, while the latter condition is desirable for maximizing source coherency in the diffraction mode.
The specimen is immersed in the next lens encountered along the column, the objective lens. The objective lens is a magnetic lens, the design of which is the most crucial of all lenses on the instrument. Instrumental resolution is limited primarily by the spherical aberration of the objective lens.

Figure 2.11: Ray diagram of Transmission Electron Microscopy (TEM).
The magnetic field at the center of the objective lens near the specimen position is large, typically 2-2.5 T (20-25 kG) [13]. This places certain restrictions on TEMs applicability to studies of magnetic materials, particularly where high spatial resolution measurements are desired. Nevertheless, low-magnification TEM is often used to study magnetic domain characteristics in magnetic materials, using so-called lorentz microscopy procedures [14]. In such instances, the objective lens is weakly excited, so that the incident electrons mainly the magnetic field due to the specimen. Changes in this field across domain boundaries produce contrast in the transmitted image. The final set of magnetic lenses beneath the specimen is jointly referred to as post-specimen lenses. Their primary task is to magnify the signal transferred by the objective lens. Modern instruments typically contain four post-specimen lenses: diffraction, intermediate, projector 1, and projector 2 (in order of appearance below the specimen). They provide a TEM with its tremendous magnification flexibility. Collectively, the post-specimen lenses serve one of two purposes: they magnify either the diffraction pattern from the sample produced at the back focal plane of the objective lens or they magnify the image produced at the image plane of objective lens. These optical planes are illustrated in the electron ray diagram in Figure 2.11. By varying the lens’s strengths so as to alternate between these two object planes, the post-specimen lenses deliver either a magnified diffraction pattern or a magnified image of the specimen to the detector.

The primary remaining considerations regarding the TEM column are the diaphragms or apertures employed at certain positions along the column. The purpose of these apertures is to filter either the source or the transmitted signal. The most important diaphragm is called the objective aperture. This aperture lies in the back focal plane of the objective lens. In this plane the scattered electron waves recombine to form a diffraction pattern. A diffraction pattern corresponds to the angular dispersion of the electron intensity removed from the incident beam by interaction with the specimen. Inserting an aperture in this plane effectively blocks certain scattered waves. The larger the objective aperture, the greater the angular dispersion that is accepted in the transmitted signal. Consequently, only intensity in the transmitted beam can contribute to the image formed at the image
plane of the objective lens. Use of a small objective aperture while operating in the image mode, which blocks all diffracted beams, can serve to enhance significantly image contrast. Use of a large objective aperture, that allows the passage of many diffracted beams, is the technique referred to as high-resolution transmission electron microscopy (HRTEM).

2.3.3 Ultra Violet-Visible (UV-Vis) Spectroscopy

Absorption spectroscopy that has the ability to measure the energy of electronic transitions and their line widths accurately, in a convenient manner, is one of the most important aspects of semiconductor characterization. The positions, particularly the band edge (which defines the band gap), are the most useful, allowing determination of alloy concentration strain, damage and identification of impurities [6].

The characteristic lines observed in the absorption (and emission) spectra of nearly isolated atoms and ions due to transitions between quantum levels are extremely sharp. As a result, their wavelengths (photon energies) can be determined with great accuracy. The lines are characteristic of a particular atom or ion and can be used for identification purposes. Positions of spectral lines can be determined with sufficient accuracy to verify the electronic structure of the molecules. The high particle density of solids, however, makes their optical spectra rather broad and often uninteresting from an experimental point of view. The large degeneracy of the atomic levels is split by inter atomic interactions into quasi continuous bands (valence and conduction bands). The energy difference between the highest lying valence band and lowest lying conduction band is designated as the fundamental band gap.

According to Bouguer-Lambert-Beer law the transmitted light intensity \( I \) through a non-reflecting medium of thickness \( t \) is given by following equation [15]

\[
I = I_o e^{-\alpha t}
\]  

(2.11)
where, $I_0$ is the incident intensity and $\alpha$ is absorption coefficient of the medium. Absorption coefficient is a measure of the energy attenuation or loss as it travels through the medium. However, if the medium is also partly reflecting with reflectance $R$ then [16]

$$I = I_0 \frac{(1-R)^2 e^{-\alpha t}}{1 - R^2 e^{-\alpha t}}$$  \hspace{1cm} (2.12)

Now from Equation 2.11 one can get absorption coefficient as

$$\alpha = \frac{2.303 \log_{10} \frac{I_0}{I}}{t} = \frac{2.303A}{t}$$  \hspace{1cm} (2.13)

The quantity $\log_{10} (I_0/I)$ is define as absorbance ($A$). Generally optical absorption spectrometer records absorbance as a function of wavelength.

For a reflecting film in the region of strong absorption (small $R$ and large $\alpha$) near the fundamental absorption edge, $\alpha$ can be calculated by

$$\alpha = \frac{2.303A}{t} + \frac{4.606 \log_{10} (1 - R)}{t}$$  \hspace{1cm} (2.14)

Here we neglected $R^2 \exp(-\alpha t)$ term in Equation 2.12. Normally, $R$ is very small near the absorption edge and therefore the second term in Equation (2.14) is neglected in determination of optical energy gap. All the important optical constants like refractive index, transmission coefficient and optical energy gap can be computed using the values of $\alpha$ or the absorbance.

**Determination of Band gap**

The major sources of absorption in solids are its electrons. Band to band transition is the main contributor to absorption processes in solid material [17]. When a photon of sufficient energy interacts with semiconducting material valance band electrons get
excited and jump to the conduction band across the forbidden energy gap. When conduction band minima and valance band maxima are at the same ‘k’, direct transition will take place and band gap can be given as

\[ E_g = E_c - E_v = h\theta = \Delta E \]  

(2.15)

For indirect transition, conduction band minima and valance band maxima are not at the same \( k \) position in \( k \)-space. The energy and momentum conservation in such a transition can be explained by the emission or absorption of a phonon (i.e. process involves a simultaneous interaction with lattice vibration [18]. For this case the energy difference can be given as

\[ \Delta E = h\theta_{\text{photon}} \pm h\theta_{\text{phonon}} \]  

(2.16)

where \( h\theta_{\text{phonon}} \) is the energy of a phonon that is absorbed (plus sign) or emitted (minus sign) simultaneously with the absorption of the photon.

Generally energy band gap is determined by plotting absorption coefficient \( \alpha \) and photon energy (for detailed see reference 19). For the present work determination of band gap energy was carried out by plotting absorbance (\( A \)) with respect to wavelength/energy of incident light.

The optical ray diagram of UV-Vis double beam spectrophotometer (PerkinElmer, Lmbda-35, U.S.A.) and UV apparatus are shown in the Figure 2.12. Spectrophotometer consists of deuterium (UV) and halogen (Visible/IR) sources, monochromator, sample containers and detectors. The electrical excitation of deuterium at low pressure produces a continuous UV spectrum in the range 160-375 nm. While, halogen lamp is used as sources of visible/IR light in the wavelength range of 350-2500 nm. The polychromatic light from the source enters the monochromator through the entrance slit1 after reflection from mirror M1 and M2 [20-21].
Figure 2.12: (a) Digital photograph of UV-Vis apparatus used for absorption study (Perkin Elmer Lambda-35 spectrophotometer) and (b) Schematic ray diagram of UV-Visible absorption spectrometer.
2.3.4 Photoluminescence Spectroscopy

Photoluminescence (PL) is a well-established, low cost and widely practiced tool for materials analysis. In the context of surface and microanalysis, PL is applied mostly qualitatively or semiquantitatively to exploit the correlation between the structure and composition of a material system and its electronic states and their lifetimes, and to identify the presence and type of trace chemicals, impurities, and defects. Sensitivity is one of the strengths of the PL technique, allowing very small quantities (nanograms) or low concentrations (parts-per-trillion) of material to be analyzed. Uses for PL are found in many fields, including environmental research, pharmaceutical and food analysis, forensics, pesticide studies, medicine, biochemistry, and semiconductors and materials research [6, 22].

Basic Principle

In PL, a material gains energy by absorbing light at some wavelength by promoting an electron from a low to a higher energy level. This may be described as making a transition from the ground state to an excited state of an atom or molecule, or from the valence band to the conduction band of a semiconductor crystal (electron-hole pair creation). The system then undergoes a nonradiative internal relaxation involving interaction with crystalline or molecular vibrational and rotational modes, and the excited electron moves to a more stable excited level, such as the bottom of the conduction band or the lowest vibrational molecular state. (See Figure 2.13) If the cross-coupling is strong enough this may include a transition to a lower electronic level, such as an excited triplet state, a lower energy indirect conduction band, or a localized impurity level. A common occurrence in insulators and semiconductors is the formation of a bound state between an electron and a hole (called an exciton) or involving a defect or impurity (electron bound to acceptor, exciton bound to vacancy, etc.). After a system-dependent characteristic lifetime in the excited state, which may last from picoseconds to many seconds, the electronic system will return to the ground state. In luminescent materials some or all of
the energy released during this final transition is in the form of light, in which case the relaxation is said to be radiative. The wavelength of this emission is longer than that of the incident light. This emitted light is detected as photoluminescence, and the spectral dependence of its intensity is analyzed to provide information about the properties of the material. The time dependence of the emission can also be measured to provide information about energy level coupling and lifetimes.

**Figure 2.13:** Schematic of PL from the standpoint of semiconductor or crystalline systems (left) and molecular systems (right).

**Salient Features**

Since the excited electronic distribution approaches thermal equilibrium with the lattice before recombining, only features within an energy range of $kT$ of the lowest excited level (the band edge in semiconductors) are seen in a typical PL emission spectrum. It is possible, however, to monitor the intensity of the PL as a function of the wavelength of the incident light. In this way the emission is used as a probe of the absorption, showing additional energy levels above the band gap.
Scanning a range of wavelengths gives an emission spectrum that is characterized by the intensity, line shape, line width, number, and energy of the spectral peaks. Depending on the desired information, several spectra may be taken as a function of some external perturbation on the sample, such as temperature, pressure, or doping variation, magnetic or electric field, or polarization and direction of the incident or emitted light relative to the crystal axes. The features of the spectrum are then converted into sample parameters using an appropriate model of the PL process. A sampling of some of the information derived from spectral features is given in Table 2.2.

A wide variety of different mechanisms may participate in the PL process and influence the interpretation of a spectrum. At room temperature, PL emission is thermally broadened. As the temperature is lowered, features tend to become sharper, and PL is often stronger due to fewer nonradiative channels. Low temperatures are typically used to study phosphorescence in organic materials or to identify particular impurities in semiconductors [23].

**Working of Photoluminescence**

The room-temperature photoluminescence (PL) measurements were carried out by a Horiba Jobin Yvon Fluorolog 3 spectrofluorometer using a Xe lamp as the excitation source. The typical measurement procedure is shown in Figure 2.14 (b). For excitation, a lamp delivers a broad band radiation spectrum from 200 to 1500 nm with maximum intensity between 250 and 650 nm. The same wavelength range is used for excitation in typical fluorescence applications. For excitation, typically a narrow part of this wavelength range is selected and guided to the sample box by a double monochromator system. The monochromator further enables a high noise reduction and thus a signal to noise ratio better than 4000. The spectral line width of the excitation is 5 nm FWHM (full width at half maximum). The modular setup of this equipment allows an easy change of the excitation source. For emission detection, one can choose between UV/Vis and IR-channel. For UV/Vis detection a photo multiplier is used, whereas the IR-detection is based on a germanium detector. Alternatively, pulsed excitation and a corresponding
detection are also possible. The detection efficiency not only depends on the excitation, but also on the proper choice of sample geometry as well as cut-off filters settings. The latter are required to cut off the excitation wavelengths. The slit widths may be varied to give resolutions between 2.5 nm to 20 nm for the emission monochromator and between 2.5 nm to 15 nm for the excitation monochromator and in increments of 0.1 nm [24].

Table 2.2: Some selective parameters that can extracted from Photoluminescence spectroscopy [6].

<table>
<thead>
<tr>
<th>Spectral feature</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Peak Energy</strong></td>
<td>Compound identification</td>
</tr>
<tr>
<td></td>
<td>Band gap /electronic levels</td>
</tr>
<tr>
<td></td>
<td>Impurity or exciton binding energy</td>
</tr>
<tr>
<td></td>
<td>Quantum well width</td>
</tr>
<tr>
<td></td>
<td>Impurity species</td>
</tr>
<tr>
<td></td>
<td>Alloy composition</td>
</tr>
<tr>
<td></td>
<td>Internal strain</td>
</tr>
<tr>
<td></td>
<td>Fermi energy</td>
</tr>
<tr>
<td><strong>Peak Width</strong></td>
<td>Structural and chemical &quot;quality&quot;</td>
</tr>
<tr>
<td></td>
<td>Quantum well interface roughness</td>
</tr>
<tr>
<td></td>
<td>Carrier or doping density</td>
</tr>
<tr>
<td><strong>Slope of high-energy tail</strong></td>
<td>Electron temperature</td>
</tr>
<tr>
<td><strong>Polarization</strong></td>
<td>Rotational relaxation times</td>
</tr>
<tr>
<td></td>
<td>Viscosity</td>
</tr>
<tr>
<td><strong>Peak intensity</strong></td>
<td>Relative quantity</td>
</tr>
<tr>
<td></td>
<td>Molecular weight</td>
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<tr>
<td></td>
<td>Polymer conformation</td>
</tr>
<tr>
<td></td>
<td>Excited state lifetime</td>
</tr>
<tr>
<td></td>
<td>Radiative efficiency</td>
</tr>
<tr>
<td></td>
<td>Impurity or defect concentration</td>
</tr>
</tbody>
</table>
Figure 2.14: (a) Digital photograph of Horiba Jobin Yvon Fluorolog 3 spectrofluorometer used in present study and (b) Setup of the PL spectrometer Jobin Yvon Fluorolog 3. The arrangement allows flexibility in geometry and excitation source. Due to the double monochromator concept no filters are required.
2.3.5 Raman Spectroscopy

Raman spectroscopy is a very convenient technique for the identification of crystalline or molecular phases, for obtaining structural information on noncrystalline solids, for identifying molecular species in aqueous solutions, and for characterizing solid-liquid interfaces. Backscattering geometries, especially with micro focus instruments, allow films, coatings, and surfaces to be easily measured. Ambient atmospheres can be used and no special sample preparation is needed. In-situ Raman measurements have become more important in many types of vapor and liquid deposition systems, as it is important to monitor the progress of reactions and changes in structure as films or crystals are grown. Fiber optic cables, sapphire light pipes and other optical systems are available for bringing the laser beam into the reaction chamber and for collecting the scattered light. Spectra can be collected without disturbing the deposition process [25].

Raman peaks are sensitive to hydrostatic pressure, presence of impurity, chemical composition and phase. Raman scattering is also a useful tool to study the dynamics of structure by analyzing the characteristic modes associated with nano regions. The selection rules are very sensitive to the local and global symmetries. In crystalline solids, the Raman effect deals with phonons, instead of molecular vibrations. The fundamental requirement of a phonon to be Raman active is that the first derivative of the polarizability with respect to the vibrational normal coordinate has a non-zero value.

Basic Principle

Raman spectroscopy is a technique based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample [26]. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman Effect. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. The Raman effect is based on molecular
deformations in electric field $E$ determined by molecular polarizability $\alpha$. The laser beam can be considered as an oscillating electromagnetic wave with electrical vector $E$. After interaction with the sample it induces electric dipole moment $P = \alpha E$ which deforms molecules. Because of periodical deformation, molecules start vibrating with characteristic frequency $\nu_m$.

Amplitude of vibration is called a nuclear displacement. In other words, monochromatic laser light with frequency $\nu_0$ excites molecules and transforms them into oscillating dipoles. Such oscillating dipoles emit light of three different frequencies (Figure 2.15) when:

(a) A molecule with no Raman-active modes absorbs a photon with the frequency $\nu_0$. The excited molecule returns back to the same basic vibrational state and emits light with the same frequency $\nu_0$ as an excitation source. This type of interaction is called an elastic Rayleigh scattering.

(b) A photon with frequency $\nu_0$ is absorbed by Raman-active molecule which at the time of interaction is in the basic vibrational state. Part of the photon’s energy is transferred to the Raman-active mode with frequency $\nu_m$ and the resulting frequency of scattered light is reduced to $\nu_0 - \nu_m$. This Raman frequency is called Stokes frequency, or just “Stokes”.

(c) A photon with frequency $\nu_0$ is absorbed by a Raman-active molecule, which, at the time of interaction is already in the excited vibrational state. Excessive energy of excited Raman active mode is released, molecule returns to the basic vibrational state and the resulting frequency of scattered light goes up to $\nu_0 + \nu_m$. This Raman frequency is called Anti- Stokes frequency, or just “Anti-Stokes”.

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A Raman system typically consists of the following four major components [27]:

1. Excitation source (Laser).
2. Sample illumination system and light collection optics.
3. Wavelength selector (Filter or Spectrophotometer).
4. Detector (Photodiode array, CCD or PMT).

A sample is normally illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is collected with a lens and is sent through an interference filter or spectrophotometer to obtain Raman spectrum of a sample. Since spontaneous Raman scattering is very weak, the main difficulty of Raman spectroscopy is

**Figure 2.15:** Schematic diagram of transition in molecule.

**Instrumentation**

A Raman system typically consists of the following four major components [27]:

1. Excitation source (Laser).
2. Sample illumination system and light collection optics.
3. Wavelength selector (Filter or Spectrophotometer).
4. Detector (Photodiode array, CCD or PMT).

A sample is normally illuminated with a laser beam in the ultraviolet (UV), visible (Vis) or near infrared (NIR) range. Scattered light is collected with a lens and is sent through an interference filter or spectrophotometer to obtain Raman spectrum of a sample. Since spontaneous Raman scattering is very weak, the main difficulty of Raman spectroscopy is
separating it from the intense Rayleigh scattering. More precisely, the major problem here is not the Rayleigh scattering itself, but the fact that the intensity of stray light from the Rayleigh scattering may greatly exceed the intensity of the useful Raman signal in the close proximity to the laser wavelength. In many cases the problem is resolved by simply cutting off the spectral range close to the laser line where the stray light has the most prominent effect. Very strong laser pulse with electric field strength > 109 Vcm\(^{-1}\) transforms up to 50% of all laser pulse energy into coherent beam at Stokes frequency \(\nu_0 - \nu_m\) (Figure 2.15). The Stokes beam is unidirectional with the incident laser beam. Only the mode which is the strongest in the regular Raman spectrum is greatly amplified. All other, weaker Raman active modes are not present. The Stokes frequency is so strong that it acts as a secondary excitation source and generates the second Stokes line with frequency \(\nu_0 - 2\nu_m\). The second Stokes line generates the third one with the frequency \(\nu_0 - 3\nu_m\) and so on. Stimulated Raman technique enjoys 4 – 5 orders of magnitude enhancement of Raman signal as compared to the spontaneous Raman scattering. Notch filters cut-off spectral range of ± 80 - 120 cm\(^{-1}\) from the laser line. This method is efficient in stray light elimination but it does not allow detection of low-frequency Raman modes in the range below 100 cm\(^{-1}\). Stray light is generated in the spectrometer mainly upon light dispersion on gratings and strongly depends on grating quality. Raman spectrometers typically use holographic gratings which normally have much less manufacturing defects in their structure than the ruled ones. Stray light produced by holographic gratings is about an order of magnitude less intense then from ruled gratings of the same groove density. Using multiple dispersion stages is another way of stray light reduction. Double and triple spectrometers allow taking Raman spectra without use of notch filters. In such systems Raman-active modes with frequencies as low as 3 – 5 cm\(^{-1}\) can be efficiently detected.
2.3.6 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is a widely used surface analytical technique. SEM, accompanied by X-ray analysis, is considered to be a relatively rapid, inexpensive, and basically non-destructive approach for surface analysis. High resolution images of surface topography, with excellent depth of field are produced using a highly-focused, scanning (primary) electron beam. SEM system used for taking morphology in this study is shown in Figure 2.17.

The Scanning Electron Microscope system consist the electron column and control console. The schematic ray diagram of SEM is shown in Figure 2.18. The electron column consists of the electron source, the magnetic focusing lenses (condenser lenses, objective lenses), apertures, scan coils, the sample vacuum chamber and stage region at the bottom of the column and the electronics console containing a cathode ray tube.

Figure 2.16: The Raman microscope (Model: Renishaw inVia) used in present thesis.
(CRT) viewing screen, knobs and computer keyboard that control the electron beam and the scanning modules [29-32].

![Image of Scanning Electron Microscope and EDAX setup](image)

**Figure 2.17:** Digital photograph of Scanning Electron Microscope and EDAX setup used in present work.

The electron gun generates electrons and accelerates them to energy in the range 0.1-30 keV. The spot size from tungsten/LaB₆ gun is too large to produce a sharp image unless electron lenses are used to de magnify it and place a much smaller focused electron spot on the specimen. The condenser lens control determines the available beam current and the minimum beam size and the objective lens control allows the beam to be focused so that the smallest diameter is located exactly at the specimen surface. When the incident electrons penetrate the surface a number of interactions occur that can results in the emission of electrons or photons from (or through) the surface. A reasonable fraction of the electrons emitted can be collected by appropriate detectors and the output can be used to modulate the brightness of a cathode ray tube (CRT) whose x- and y- inputs are driven in synchronism with the x-y voltages rastering the electron beam. In this way, every point
of that the beam strikes on the sample is mapped directly onto a corresponding point the screen [28-29]. There are three types of principle images produced in the SEM

[i] Secondary electron images

[ii] Backscattered electron images and

[iii] Elemental X-ray maps

Figure 2.18: Schematic diagram of Scanning Electron Microscopy (SEM).

2.3.7 Energy Dispersive X-ray Spectroscopy (EDAX)

Energy dispersive X-ray analysis, also known as EDS, EDX or EDAX, is a technique used to identify the elemental composition of a sample. During EDS, a sample is exposed to an electron beam inside a scanning electron microscopy (SEM) or transmission electron microscopy (TEM). These electrons collide with the electrons within the sample, causing some of them to be knocked out of their orbits. The vacated positions are filled by higher energy electrons which emit X-rays in the process (Figure 2.19). By analyzing
the emitted X-rays, the elemental composition of the sample can be determined. EDS is a very handy tool for performing the constitutional analysis of any kind of material [33-34]. In the present study the EDS is used with SEM is shown in Figure 2.17.

![Figure 2.19: A schematic representation showing how X-rays are produced which are used by the EDAX to analyze samples.](image)

### 2.3.8 Thermal Analysis

Thermal analysis techniques measure the change in physical and chemical properties of a substance as a function of temperature, while the substance is subjected to a controlled temperature programme.

**Thermal Gravimetric Analysis (TGA)** is a simple analytical technique that measures the weight loss (or weight gain) of a material as a function of temperature. TGA is also very useful to determine oxidation temperature. As materials are heated, they can lose weight from a simple process such as drying, or from chemical reactions that liberate gasses. Some materials can also gain weight by reacting with the atmosphere in the testing environment.
Differential Thermal Analysis (DTA): In DTA, the instrument monitors the difference in temperature between the sample under study and an inert reference material. The difference in temperature is observed when there is emission (exothermic) or absorption (endothermic) of heat due to a chemical reaction, phase or structure changes occurring in the sample. A peak or a dip of the straight baseline indicates whether the process is exothermic or endothermic respectively [35].

Differential Scanning Calorimetry (DSC) is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature whilst the substance and reference material are subjected to a controlled temperature programme. DSC defines the glass transition as a change in the heat capacity as the polymer matrix goes from the glass state to the rubber state. This is a second order endothermic transition (requires heat to go through the transition). So in the DSC the transition appears as a step transition and not as a peak such as might be seen with a melting transition [36].

For performing the analysis, a weighed sample of each compound (~3 - 4 mg) was loaded onto alumina pans, and heated at a rate of 5 to 10 °C min$^{-1}$ to 100-900 °C in air or under flowing nitrogen gas (20 ml/min) on a TA Instruments SDT Q Series 600.

Figure 2.20: Digital photograph of DSC instrument (TA Instruments SDT Q Series 600).
Chapter 2: Theoretical Background Experimental Techniques

2.4 References

[27] www.princeton instruments.com