Chapter 2

Experimental techniques and tools used for the synthesis and characterization of the nanomaterials
2.1. Introduction

Nanotechnology is a very diverse field, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly. It is orienting at developing new materials with dimensions on the nanoscale and investigating whether we can directly control matter on the atomic scale. Nanotechnology has the potential to create many new materials and devices with a vast range of applications, such as in medicine, electronics and energy production. As particle size drop from microns to tens of nanometers, nanoparticles cease to behave as bulk and begin exhibiting quantum mechanical behaviour similar to that of individual atoms. Ten hydrogen atoms stacked side-by-side measure only a single nanometer. The lure of nanotechnology is not just making small devices; but to construct the smallest physical structures possible.

The goal of molecular manufacturing is to manipulate atoms individually and place them in a pattern to produce a desired structure. Experts sometimes disagree about what constitutes the nanoscale; but in general, you can think of nanotechnology dealing with anything measuring between 1 and 100 nm. Unusual physical, chemical and biological properties can emerge in materials at the nanoscale. These properties may differ in important ways from the properties of bulk materials or single atoms or molecules. A single atom is only a tenth of a nanometer in diameter.
Nanotechnology is, in a very literal sense, an opportunity to play with,

(1) Physical methods and

(2) Chemical methods to synthesise nanostructures.

Several different physical methods are currently in use for the synthesis and commercial production of nanostructured materials. The first and the most widely used technique involves the synthesis of single-phase metals and ceramic oxides by the inert-gas evaporation technique [1]. The generation of atom clusters by gas phase condensation [2] proceeds by evaporating a precursor material, either a single metal [3] or a compound [4], in a gas maintained at a low pressure, usually below 1 atm. The evaporated atoms or molecules undergo a homogeneous condensation to form atom clusters via collisions with gas atoms or molecules in the vicinity of a cold-powder collection surface. The clusters once formed must be removed from the region of deposition to prevent further aggregation and coalescence of the clusters. These clusters are readily removed from gas condensation chamber either by natural convection of the gas or by forced gas flow.

Sputtering is another technique used to produce nanostructured materials clusters as well as a variety of thin films [5]. This method involves the ejection of atoms or clusters of designated materials by subjecting them to an accelerated and highly focused beam of inert gas such as argon or helium. The third physical method involves the generation of nanostructured materials via severe mechanical deformation [6, 7]. In this method nanostructured materials are produced not by cluster assembly but
rather by structural degradation of coarser-grained structures induced by the application of high mechanical energy. The nanometer-sized grains nucleate within the shear bands of the deformed materials converting a coarse-grained structure to an ultrafine powder. The heavy deformation of the coarser materials is affected by means of a high-energy ball mill or a high-energy shear process. Although this method is very useful in generating commercial quantities of the material, it suffers from the disadvantage of contamination problems resulting from the sources of the grinding media.

Self-assembled quantum dots nucleate spontaneously under certain conditions during molecular beam epitaxy [MBE] \[8\] and metalorganic vapour phase epitaxy [MOVPE] \[9\], when a material is grown on a substrate to which it is not lattice matched. The resulting strain produces coherently strained islands on top of a two dimensional “wetting layer”. This growth mode is known as Stranski-Krastanov growth \[10\]. The islands can be subsequently buried to form the quantum dot. This fabrication method has potential applications in quantum cryptography \[11\] (i.e. single photon sources) and quantum computation \[12\]. The main limitations of this method are the cost of fabrication and the lack of control over positioning of individual dots. The major two methods involved in the present thesis for the synthesis of nanostructured materials are liquid phase pulsed laser ablation (LP-PLA) and wet chemical methods. Controllable growth of flexible nanoparticles embedded polymeric optical devices can be fabricated at a very low cost through these two methods.
2.2. Liquid phase pulsed laser ablation (LP-PLA)

Formation of nanoparticles using pulsed laser ablation of solids, either in gas or in vacuum, has been extensively explored during the last decade for nanofabrication such as nanostructured thin films, nanorods [13], quantum wells and quantum dots [14]. Being performed in a controllable contamination-free environment this method makes possible the production of nanomaterials without impurities. Precise control over the size of the nanostructures could be attained by tuning various deposition parameters like substrate temperature, substrate to target distance, gaseous atmosphere in the chamber and laser energy density during the pulsed laser deposition [15].

Recently liquid phase-pulsed laser ablation technique (LP-PLA) has been evolved as a synthesis technique for the preparation of nanoparticles [16]. Liquid phase pulsed laser ablation (LP-PLA) involves the focusing of high intense laser beam (UV nanosecond pulsed laser source such as the frequency tripled (355 nm) or quadrupled (266 nm) solid state Nd:YAG laser or the KrF (248 nm) or ArF (193 nm) excimer laser) onto the surface of a solid target, which is submerged beneath a liquid (in the present work water) as shown in figure 2.1.
Figure 2.1. The setup of liquid phase pulsed laser ablation.

The very first process of liquid phase pulsed laser ablation is the interaction of laser with the solid target surface submerged below the liquid layer and subsequent vaporisation of the solid target as well as a very small amount of surrounding liquid. At sufficiently high incident flux densities and short pulse duration, all elements in the target are rapidly heated up to their evaporation temperature due to pulsed laser irradiation. It leads to the congruent evaporation of the target irrespective of the evaporating point of the constituent elements or compounds of the target. Materials are dissociated from the target surface and ablated out with the same stoichiometry as the target leading to plasma plume formation from the surface of the material. The species in the plasma plume will undergo rapid collision with the molecules of the surrounding liquid and react them,
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producing new compounds containing atoms from both the original target and the liquid.

Since the ejected species are in highly excited state, there is strong chance for the chemical reactions between the ablated species and molecules in the liquid [17]. Typically the reaction products are nanoparticles consisting of atoms from both the target and the liquid, which will form nanoparticle suspension in the liquid. These nanoparticles accumulate homogenously in the surrounding liquid thus forming a colloidal solution. Therefore there is a chance for the prolonged interaction of this nanocolloidal suspension with the laser radiation leading to further changes in the nanoparticle's composition, size or morphology [18].

Thus we can see that the process of laser interaction with the target is similar for both laser ablation in vacuum and ablation at the solid-liquid interface. In both process plasma plume will be generated and create a strong confinement of the emission species, resulting in an efficient electron-ion recombination. The major difference is that when the plasma begins to expand, which occurs freely in vacuum in normal PLA where as it is confined by a liquid layer in LP-PLA. The liquid layer causes delay to the expansion of the plasma that will lead to a very high plasma pressure and temperature thus allowing the formation of novel materials.

Fabbro et al [19] reported that at the very initial stage of interaction of the high energy laser with the interface between the solid and the liquid, species ejected from the solid target surface have a large initial kinetic energy. The liquid surroundings will generate a covering effect to these
ejected species and the species will form a dense region in the vicinity of the solid-liquid interface. This stage is similar to that which occurs in vacuum or low pressure gas, where the laser generates a plasma 'plume'. In LP-PLA, the plasma is confined in the liquid and expansion process happens adiabatically at supersonic velocity generating a shock-wave in front of it. This shock-wave will cause an additional instantaneous pressure as it passes through the liquid. This 'laser-induced pressure' will result in the temperature increase in the plasma [20, 21]. This is another reason for the higher pressure and higher density in the case of plasma formed in LP-PLA compared with PLA plasma formed in gas or vacuum.

Detailed studies regarding the mechanisms involved in the nucleation and phase transition of nanocrystals upon LP-PLA are not reported yet. The nucleation thermodynamics, the phase transition and the growth kinetics of nanocrystals by laser ablation of liquids is explained well in a recent review by Yang et al [22]. It is proposed that LP-PLA is very fast and far from equilibrium process. Hence all metastable and stable phases forming at the initial, intermediate and final stages of the transformation must be reserved in the final products especially for any metastable intermediate phases [23]. It has been recently demonstrated [24, 25] that the nanoparticle size can be drastically reduced by the use of aqueous solutions. Gold as well as ZnO nanoparticles [26, 27] dispersed water can be prepared by this method using third harmonic Nd: YAG laser.

One of the advantages of LP-PLA is that both the solid target and the liquid are vaporised, so the product will contain atoms from the target
material and the liquid. The generation of various nanoparticles by LP-PLA is an alternative to the well-known chemical vapour deposition (CVD) method and is characterized by its relative simplicity and the low cost of the experimental setup. The very special advantage of LP-PLA is that nanoparticles produced by laser ablation of solid targets in a liquid environment are free of any counter-ions or surface-active substances because quantum dots can be directly dispersed in liquid medium without the play of much chemistry [28]. However, physical aspects of laser ablation in liquids still remain unclear and relative contributions of the physical and chemical factors of particle reduction are to be still evaluated.

2.2.1. Water Confined Regime (WCR) model

The plasma production in LP-PLA is associated with the shock wave emission [29]. It has been reported that the ablation rate is high in the water confined regime as compared to the ambient conditions [22]. In the WCR configuration water confined plasma exerts a much stronger pressure. This enhanced pressure has significant effects on the mechanical response of solid surfaces immersed in the liquid. This high-pressure, high-temperature plasma results in a much higher ablation rate. The duration of the shock wave is two to three times longer than that in the direct regime for the same laser intensity.

Here the target material is put in a glass jar with a water layer with an appropriate thickness above the target. It has been reported that the ablation rate could be highly enhanced in the WCR regime by a 1.1 mm water layer above the solid substrates as reported on Si substrate in water media [30].
The energy absorbed by the target material decreases quickly with the increase of the water layer thickness. Therefore, the plasma generated in water is weaker and the ablation rate decreases accordingly. With the increase of water layer thickness, the plasma became weaker and finally almost disappeared. Hence the thickness of the water layer should be minimum for efficient ablation rate.

Also the thickness of the water layer must not fall very low since it may lead to ablative piston effect. The removal of the material during laser ablation will lead to a rapid rise in the local particle density, which results in a rapid rise in the pressure of the materials’ surface. This process is usually accompanied by plasma generation and the high pressure is released as a shock wave. After emitting into air, the shock wave will decay into acoustic waves by air friction, which is called the “ablative piston” effect [31]. When there is a water layer above the surface of the target, the shock wave generated during laser ablation will be emitted into the water layer first and the plasma will produce an explosion in water. Afterwards, the shock wave will decay into acoustic waves as a direct result of air friction. Therefore when the water layer thickness above the surface of the target is very small, the material removal rate will be very large and the ablative piston effect will be predominant in the ablation process.

We know that the pressure developed in the liquid confined ablation mode will be very high. An analytical model was previously introduced for the prediction of laser-induced pressures in the confined ablation mode [32]. According to this model there exist three different phases for the plasma;
laser heating, adiabatic cooling and final expansion. This model helps in the
direct estimation of the pressure inside the confined plasma. This maximum
pressure generated by the laser plasma in the WCR is given by the following
relation [32],

$$P(GPa) = 0.01 \sqrt{\frac{\alpha}{\alpha + 3}} \times \sqrt{Z (gcm^{-2}s^{-1})} \times \sqrt{I_0 (GW/cm^2)} \quad (2.1)$$

where $I_0$ the incident power intensity, $\alpha$ is the fraction of internal
energy devoted to thermal energy (typically $\alpha = 0.25$) and $Z$ the reduced
shock impedance between target and the confining water defined by the
relation,

$$\frac{2}{Z} = \frac{1}{Z_{\text{water}}} + \frac{1}{Z_{\text{target}}} \quad (2.2)$$

where $Z_{\text{water}}$ and $Z_{\text{target}}$ are the shock impedances of the water and the
target respectively. The maximum pressure obtained in the water confined
regime can be compared to the value obtained in the direct ablation regime.
In the direct ablation regime under ambient conditions, the ablation pressure
is given by the relation,

$$P_d (GPa) = 0.4 I_0^{0.7} (GW/cm^2) \lambda^{-0.03} (\mu m) \tau^{-0.05} (ns) \quad (2.3)$$

where $\lambda$ is wavelength and $\tau$ pulse duration. The relation between
the saturated vapour pressure $P$ and plume temperature $T$ is given by [33],

$$P(T) = P_0 \exp \left[ - \frac{\Delta G_{iv}}{RT} \right] \quad (2.4)$$
where $P_a$ is the ambient pressure, $\Delta G_s$ and $R$ are constants. Here, the surface temperature of substrate $T_s$ is equal to plume temperature $T$ at thermal equilibrium. The ablation rate $\nu$ can be written as [34],

$$\nu = \nu_0 \exp \left( - \frac{T_s}{T_a} \right)$$  \hspace{1cm} (2.5)

where $\nu_0$ is of the order of the sound velocity within the target material and $T_a$ the activation temperature. From eqn. (2.4) it is obvious that the substrate surface temperature $T_s$ increases with plasma pressure. Also from eqn. (2.5), it is observed that higher $T_s$ results in higher ablation rate. Also the laser ablation in the water confined regime is a dynamic positive feedback process because the higher ablation rate of material will enhance the confined plasma pressure. Therefore, we can conclude that the ablation rate will be very much enhanced by WCR.

2.3. Chemical methods

Recent advances in the synthesis of various nanoparticles using colloidal chemical approaches involve either rapid injection of reagents into hot surfactant solution followed by ageing at high temperature or the mixing of reagents at a low temperature and slow heating under controlled conditions. The advantage of chemical synthesis is its versatility in designing and synthesizing new materials that can be refined into a final product. The primary advantage of the chemical processes over other methods is its good chemical homogeneity, as chemical synthesis offers mixing at the molecular level. Molecular chemistry can be designed to prepare new materials by
understanding how matter is assembled on an atomic or molecular level and the consequent effects on the desired material macroscopic properties. A basic understanding on the principles of crystal chemistry, thermodynamics and phase equilibrium and reaction kinetics is important to take advantage of the many benefits that chemical processing has to offer.

There are certain difficulties in general chemical processing. In some preparations, the chemistry is complex and hazardous. Contamination can also result from the byproducts being generated or side reactions in the chemical process. This should be minimized or avoided to obtain desirable properties in the final product. Agglomeration can also be a major cause of concern at any stage in a synthetic process and it can dramatically alter the properties of the materials. Agglomeration frequently makes it more difficult to consolidate nanoparticles to a fully dense and compact structure. Finally, although many chemical processes are scalable for economical production, it is not always straightforward for all systems.

Solution chemistry is used sometimes to prepare the precursor, which is subsequently converted to the nanophase particles by non-liquid phase chemical reactions. Precipitation of a solid from a solution is a common technique for the synthesis of fine particles. The general procedure involves reactions in the aqueous or non-aqueous solutions containing the soluble or suspended salts [1]. Once the solution becomes super saturated with the product, the precipitate is formed by either homogeneous or heterogeneous nucleation. The formation of a stable material with or without the presence of a foreign species is referred to as heterogeneous or
homogeneous nucleation respectively. The growth of the nuclei after formation usually proceeds by diffusion, where concentration gradients and reaction temperatures are very important in determining the growth rate of particles, for example to form monodispersed particles. For instance, to form unagglomerated particles with a very narrow size distribution, all the nuclei must be formed at nearly the same time and the subsequent growth must occur without further nucleation or agglomeration of particles.

Nanostructured materials are also prepared by chemical vapour deposition (CVD) [35] or chemical vapour condensation (CVC) [36] which are used to produce high-purity, high-performance solid materials. That means a chemical precursor is converted to the gas phase and it then undergoes decomposition at either low or atmospheric pressure to generate the nanostructured particles. Precursor gases (often diluted in carrier gases) are delivered into the reaction chamber at approximately ambient temperatures. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase and are deposited onto the substrate. The process is often used in the semiconductor industry to produce thin films.

Chemical vapour deposition (CVD) is a generic name for a group of processes that involve depositing a solid material from a gaseous phase and is similar in some respects to physical vapour deposition (PVD). In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile byproducts are also
produced, which are removed by gas flow through the reaction chamber. CVD is an extremely versatile process that can be used to process almost any metallic or ceramic compound. Some of these include elements, metals, alloys, carbides, nitrides, borides, oxides and intermetallic compounds. It has applications in coatings for a variety of applications such as wear resistance, corrosion resistance, high temperature protection, erosion protection etc. They also find applications in integrated circuits, sensors and optoelectronic devices, production of novel powders and fibres and optical fibres for telecommunications. The clusters prepared by these methods have poorly defined surfaces and a broad size distribution, which is detrimental to the properties of semiconductor materials. A more detailed discussion on nanomaterial preparation and nanostructure fabrication can be found in the recent literature [1].

2.3.1. Wet chemical methods

Wet chemical method is a recently introduced method which is a simple, room temperature method for the synthesis of nanostructures. Wet chemistry is a term that represents a number of scientific techniques that involve direct experimentation with liquids. Because it is a broad industry term, the exact definition will vary from business to business. A general rule that can be applied is that if it involves a scientist working with liquids by hand and physically observing the results of the experiment, it is wet chemistry. The use of robotics in the laboratory, however, has even challenged this definition to some extent.
Wet chemistry includes basic experimentation techniques like measuring, mixing and weighing chemicals, as well as testing concentration, conductivity, density, pH, specific gravity, temperature, viscosity and other aspects of liquids. Analytical techniques in wet chemistry are usually qualitative in nature, meaning that they attempt to determine the presence of a specific chemical rather than the exact amount. However, some quantitative techniques are used in wet chemistry, and they include gravimetric (weighing) and volumetric analysis (measuring).

Bench chemistry is sometimes used as a synonym for wet chemistry. The terms differ in two primary ways: first, bench chemistry can involve dry chemicals, while wet chemistry always involves at least one substance in the liquid phase; second, wet chemistry sometimes involves hightech equipment, while bench chemistry only includes techniques that use simple devices in keeping with the classical chemistry spirit. Both types of chemistry, however, do share many of the same techniques and equipment.

A large number of techniques have been used for the synthesis of semiconductor nanostructures, such as electrochemical deposition technique, sputter deposition, hydrothermal methods and vapour methods. The above said methods require reaction conditions such as high reaction temperature or accurate gas concentration, gas flow rate or scarce raw materials or complex processes and so on. Hence the wet chemistry offers simple, low temperature and environment protective method for the synthesis of the semiconductor nanoparticles.
NASA's Phoenix Mars Lander had a wet chemistry lab abroad when it landed on the red planet in 2008. As one of its experiments, Phoenix scooped up small amounts of soil, then dissolved the samples in water. The soil solutions then had various aspects tested, including conductivity, pH and redox potential. The instruments also tested for the presence of bromide anions, carbon, chloride anions, magnesium cations, oxygen, sodium cations and sulfate anions.

2.4. Characterisation tools

2.4.1. Structural characterisation

(a). X-ray diffraction studies (XRD)

Electrical and optical properties of the materials are influenced by their crystallographic nature. X-ray diffraction (XRD) studies were carried out to study the crystallographic properties of the nanostructures prepared. A given substance always produces a characteristic X-ray diffraction pattern, whether that substance is present in the pure state or as one constituent of a mixture of substances. This fact is the basis for the diffraction method of chemical analysis. The particular advantage of X-ray diffraction analysis is that it discloses the presence of a substance but not in terms of its constituent chemical elements. Diffraction analysis is useful whenever it is necessary to know the state of chemical combination of the elements involved or the particular phase in which they are present. Compared with ordinary chemical analysis, the diffraction method has the advantage that it
is much faster, requires only very small amount of sample and is non destructive [37, 38].

The basic law involved in the diffraction method of structural analysis is the Bragg’s law. When monochromatic X-rays impinge upon the atoms in a crystal lattice, each atom acts as a source of scattering. The crystal lattice acts as series of parallel reflecting planes. The intensity of the reflected beam at certain angles will be maximum when the path difference between two reflected waves from two different planes is an integral multiple of \( \lambda \). This condition is called Bragg’s law and is given by the relation,

\[
 n\lambda = 2d \sin \theta \tag{2.6}
\]

where \( n \) is the order of diffraction, \( \lambda \) is the wavelength of the X-rays, \( d \) is the spacing between consecutive parallel planes and \( \theta \) is the glancing angle (or the complement of the angle of incidence) [39]. The schematic diagram of XRD is shown in figure 2.2.
crystallographic systems can be calculated from the following equations using the (hkl) parameters and the interplanar spacing $d_{hkl}$.

For cubic system,

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$  \hspace{1cm} (2.8)

X-ray diffraction measurements of the different nanostructures were done using Rigaku automated X-ray diffractometer. The filtered copper $K\alpha$ ($\lambda=1.5418\text{Å}$) radiation was used for recording the diffraction pattern.

(b). Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is an imaging technique whereby a beam of electrons is focused onto a specimen causing an enlarged version to appear on a fluorescent screen or layer of photographic film or to be detected by a CCD camera. The first practical transmission electron microscope was built by Albert Prebus and James Hillier at the University of Toronto in 1938 using concepts developed earlier by Max Knoll and Ernst Ruska. Electrons are generated by a process known as thermionic emission in the same manner as the cathode in a cathode ray tube, or by field emission; they are then accelerated by an electric field and focused by electrical and magnetic fields onto the sample. The electrons can be focused onto the sample providing a resolution far better than that is possible with light microscopes and with improved depth of vision. Figure 2.3 shows a schematic outline of a TEM instrument. A TEM contains four parts:
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 2.2). 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.

Electromagnetic lens system

After leaving the electron source, the electron beam is tightly focused using electromagnetic lens and metal apertures. The system only allows electrons within a small energy range to pass through, so the 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. 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 works like a slide projector. A projector shines a beam of light which transmits through the slide. The patterns painted on the slide only allow certain parts of the light beam to pass through. Thus the transmitted beam replicates the patterns on the slide, forming an enlarged image of the slide when falling on the screen. TEMs work the same way except that they shine a beam of electrons (like the light in a slide projector) through the specimen (like the slide). However, in TEM, the transmission of electron beam is highly dependent on the properties of material being examined. Such properties include density, composition, etc. For example, porous material will allow more electrons to pass through while dense material will allow less. As a result, a specimen with a non-uniform density can be examined by this technique. Whatever part is transmitted is projected onto a phosphor screen for the user to see [40]. Details of a sample can be enhanced in light microscopy by the use of stains. Similarly with electron microscopy, compounds of heavy metals such as osmium, lead or uranium can be used to selectively deposit on the sample to enhance structural details. So areas where electrons are scattered appear dark on the screen, or on a positive image.

An additional class of these instruments is the electron cryomicroscope, which includes a specimen stage capable of maintaining the specimen at liquid nitrogen or liquid helium temperatures. This allows imaging specimens prepared in vitreous ice, the preferred preparation technique for imaging individual molecules or macromolecular assemblies. Another type of TEM is the scanning transmission electron microscope.
(STEM), where the beam can be rastered across the sample to form the image. In analytical TEMs, the elemental composition of the specimen can be determined by analysing its X-ray spectrum or the energy-loss spectrum of the transmitted electrons. Modern research TEMs may include aberration correctors, to reduce the amount of distortion in the image, allowing information on features on the scale of 0.1 nm to be obtained (resolutions down to 0.08 nm has been demonstrated, so far). Monochromators may also be used which reduce the energy spread of the incident electron beam to less than 0.15 eV.

From TEM images, size of the nanoparticles can be determined. Parallel lines in the high resolution transmission electron micrograph (HRTEM) represent planes in the crystal lattice and distance between them corresponds to d spacing. By comparing these d spacing values with the JCPDS data, one can identify the orientation of the planes in the synthesized material. Selective area electron diffraction (SAED) is the map of the reciprocal lattice which will also give the signature of various planes in which material has been grown. Depending on the crystalline nature of the material, the SAED pattern will be orderly arranged spots, distinguishable ring or fused rings [41]. But in the case of quantum dots concentric rings were observed in the SAED. The d spacing of the planes corresponding to the rings can be determined by the following equation,

$$dD = CL\lambda$$

(2.9)

where $L$ is the effective camera length, $\lambda$ is the de Broglie wavelength of the accelerated electrons, $D$ is the ring diameter of the electron diffraction
(STEM), where the beam can be rastered across the sample to form the image. In analytical TEMs, the elemental composition of the specimen can be determined by analysing its X-ray spectrum or the energy-loss spectrum of the transmitted electrons. Modern research TEMs may include aberration correctors, to reduce the amount of distortion in the image, allowing information on features on the scale of 0.1 nm to be obtained (resolutions down to 0.08 nm has been demonstrated, so far). Monochromators may also be used which reduce the energy spread of the incident electron beam to less than 0.15 eV.

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pattern and \( d \) is the interplanar spacing [40]. The term in the right hand side of the eqn.2.9 is referred to as the camera constant. TEM, JEOL operating at an accelerating voltage of 200 kV was used for the determination of the particle size and crystalline nature of the nanoparticles in the present work.

2.4.2. Optical studies

In the present study, diffuse reflectance spectroscopy and optical absorption spectroscopy were the optical characterization tools to determine the band gap of powder and solution samples respectively.

(a). Diffuse reflectance spectroscopy (DRS)

Diffuse reflection is the reflection of light from an uneven or granular surface such that an incident ray is seemingly reflected at a number of angles. Diffuse reflected rays from a sample do not obey the Snell’s law as do the ordinary mirror-like specular reflections. The measurement of radiation diffusely reflected from a surface constitutes the area of spectroscopy known as diffuse reflectance spectroscopy (DRS). Specular reflection is due to the reflection at the surface of single crystallites while diffuse reflection arises from the radiation penetrating into the interior of the solid and re-emerging to the surface after being scattered numerous times. Thus, the DRS spectra will exhibit both absorbance and reflectance features due to contributions from transmission, internal and specular reflectance components as well as scattering phenomena in the collected radiation.

Based on the optical properties of the sample, several models have been proposed to describe the diffuse reflectance phenomena. The Kubelka-
Munk (KM) model put forward in 1931 [42, 43] is widely used and accepted in DRS. The KM theory is based on a continuum model where reflectance properties are described by differential equations for infinitesimally small layers. When the depth of the sample is infinite, the theory is solved to arrive at the remission function or the so-called KM function \( f(r_a) \),

\[
f(r_a) = \frac{(1-r_a)^2}{2r_a} = \frac{k}{s} \tag{2.10}
\]

where, \( r_a = \frac{R_a (\text{Sample})}{R_a (\text{Standard})} \), \( R_a \) denotes the diffuse reflectance.

Here the standard used is BaSO\(_4\). \( R \) (standard) is taken as unity. The intensity of the diffusely reflected light therefore depends on the scattering coefficient \( s \) and the absorption coefficient \( k \). The band gap is estimated from the plot of \( \{(k/s, \text{hv})\} \) versus hv.

(b). Optical absorption spectroscopy

Intrinsic optical absorption of a single photon across the band gap is the dominant optical absorption process in a semiconductor. The absorption/transmission of thin films as well as colloidal solutions in the present study were recorded using Jasco V570 spectrophotometer. The block diagram of the spectrophotometer while taking the absorption of a solution is shown in figure 2.4. The spectrophotometer uses two light sources, a deuterium (D2) lamp for ultraviolet light and a tungsten (W) lamp for visible light. After bouncing off a mirror (mirror 1), the light beam passes through a slit and hits a diffraction grating. The grating can be rotated allowing for a specific wavelength to be selected. At any specific orientation
When the energy of the incident photon \( (h\nu) \) is larger than the band gap energy, the excitation of electrons from the valence band to the empty states of the conduction band occurs. The light passing through the material is then absorbed and the number of electron hole pairs generated depends on the number of incident photons \( S_0(\nu) \) (per unit area, unit time and unit energy). The frequency \( \nu \) is related to the wavelength \( \lambda \) by the relation,

\[
\lambda = \frac{c}{\nu}, \quad \text{where } c \text{ is the velocity of light.}
\]

The photon flux \( S(x,\nu) \) decreases exponentially inside the crystal according to the relation,

\[
S(x,\nu) = S_0(\nu) \exp(-ax)
\]  

where, the absorption coefficient \( \alpha \), \( (\alpha(\nu) = 4\pi kV/c) \) is determined by the absorption process in semiconductors and \( k \) is the extinction coefficient. For the parabolic band structure, the relation between the absorption coefficient \( (\alpha) \) and the band gap of the material is given by [44],

\[
\frac{\alpha h \nu}{A} = (h \nu - E_g)^r
\]

where, \( r = 1/2 \) for allowed direct transitions, \( r = 2 \) for allowed indirect transitions, \( r = 3 \) for forbidden indirect transitions and \( r = 3/2 \) for forbidden direct transitions. “A” is the parameter which depends on the transition probability. The absorption coefficient can be deduced from the absorption or transmission spectra using the relation,
\[ \alpha = \frac{1}{t} \ln\left( \frac{I}{I_0} \right) \]  

(2.13)

where, \( I \) is the transmitted intensity and \( I_0 \) is the incident intensity of the light and \( t \) is the thickness of the film. In the case of direct transition, from eqn. 2.12, \((\alpha \nu)^2\) will show a linear dependence on the photon energy \((\nu)\). A plot of \((\alpha \nu)^2\) against \(\nu\) will be a straight line and the intercept on energy axis at \((\alpha \nu)^2\) equal to zero will give the band gap energy. Thus UV-visible absorption is a simpler method of measuring the band gap of the sample material.

2.4.3. Photoluminescence studies (PL)

Photoluminescence spectroscopy is a contactless, non-destructive method of probing the electronic structure of materials [45]. Photoluminescence (PL) is the emission of light when a substance is irradiated with a shorter wavelength light. Quantum mechanically, photoexcitation causes electrons within the material to move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released radiatively or non radiatively. The radiative emission on photo-excitation is referred to as photoluminescence.

The energy of the emitted light relates to the difference in energy levels between the two electronic states involved in the transition. The quantity of the emitted light is related to the relative contribution of the radiative process. The intensity and spectral content of the luminous output is a direct measure of various important material properties. 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.

Two types of luminescence spectra can be distinguished: excitation and emission. The excitation spectrum gives the intensity variations of the exciting radiation over a range for a fixed emission wavelength. It gives information on the position of excited states just as the absorption spectrum does, except that the former reveals only the absorption bands that result in the emission of light. The observed differences between the absorption and excitation spectra can yield useful information. An emission spectrum provides information on the spectral distribution of the light emitted by a sample for a given excitation wavelength. The time resolved PL measurement is a powerful tool for the determination of the radiative efficiency that specifies the fraction of excited states which de-excite by emitting photons.

The schematic block diagram showing the components of spectrofluorometer is shown in figure 2.5. The emission and excitation spectra of the samples are recorded using Fluoromax -3 spectrofluorometer consisting of 150W Xenon arc lamp, monochromator and a detector. A continuous source of light shines on to an excitation monochromator, which selects a band of wavelengths. This monochromatic excitation light is directed onto a sample, which emits luminescence. The luminescence is directed to a second emission monochromator which selects a band of wavelengths and shines them onto a photon counting detector (R928P
2.4.4. Inductively coupled plasma - Atomic emission spectroscopy (ICP-AES)

Inductively coupled plasma atomic emission spectroscopy (ICP-AES), also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES), is a spectrophotometric technique, exploiting the fact that excited electrons emit energy at a given wavelength as they return to ground state [46]. This technique uses plasma called inductively coupled plasma to produce excited atoms. The fundamental characteristic of this process is that each element emits energy at specific wavelengths peculiar to its chemical character. Although each element emits energy at multiple wavelengths, in the ICP-AES technique it is most common to select a single wavelength (or a very few) for a given element. The intensity of the energy emitted at the chosen wavelength is proportional to the amount (concentration) of that element in the analyzed sample. Thus, by determining which wavelengths are emitted by a sample and by determining their intensities, the analyst can quantify the elemental composition of the given sample relative to a reference standard. ICP-AES measurement was done in the present work using Thermo Electron IRIS INTREPID II XSP DUO.

2.4.5. Raman spectroscopy

Raman spectroscopy is a technique that can detect both organic and inorganic species and measure the crystallinity of solids. Raman spectroscopy is based on the Raman effect, first reported by Raman in 1928 [47]. If the incident photon imparts part of its energy to the lattice in the
form of a phonon it emerges as a lower energy photon. This down converted frequency shift is known as Stokes-shifted scattering. Anti-Stokes shifted scattering results when the photon absorbs a phonon and emerges with higher energy. The anti-Stokes mode is much weaker than the Stokes mode so the Stokes-mode scattering is usually monitored. In Raman spectroscopy, a laser beam, referred to as the pump, is incident on the sample. The weak scattered light or the Raman signal is passed through a double monochromator to reject the Raleigh scattered light and the Raman shifted wavelengths are detected by a photodetector. Various properties of the semiconductors, mainly composition and crystal structure can be determined. The Stokes line shifts and broadenings becomes asymmetric for microcrystalline Si with grain sizes below 10 nm [48]. The lines become very broad for amorphous semiconductors, allowing distinction to be made between single crystal, polycrystalline, and amorphous materials. Raman spectroscopy is used to study the vibrational properties of nanostructured materials. The information about structure, phase, grain size, phonon confinement etc can be obtained from Raman spectroscopy. The extent of phonon confinement in a material can be observed as the shift in Raman line frequencies. Acoustic modes are not observed by Raman measurements in bulk systems because of their low frequencies. But in nanostructured materials, they appear in the measurable frequency range (below 100 cm⁻¹) [49, 50]. The frequency of the acoustic mode is inversely proportional to the size of the nanoparticles and this can be used to determine the size of the particles. Confinement of optical phonons results in the frequency shift and
asymmetrical broadening of longitudinal optical (LO) and transverse optical (TO) mode line shape [51]. The information about the structure and quality of the low dimensional structures can be obtained from Raman spectroscopy. In the present work, Raman studies were carried out with micro Raman (Renishaw) with He-Ne Laser (632.8 nm) as the excitation source.

2.4.6. Atomic absorption spectroscopy (AAS)

In analytical chemistry, atomic absorption spectroscopy is a technique for determining the concentration of a particular metal element in a sample [52]. The technique can be used to analyze the concentration of over 70 different metals in a solution. Although atomic absorption spectroscopy dates to the nineteenth century, the modern form was largely developed during the 1950s by a team of Australian chemists. They were led by Alan Walsh and worked at the CSIRO (Commonwealth Science and Industry Research Organisation) Division of Chemical Physics in Melbourne, Australia.

The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It relies therefore heavily on Beer-Lambert law. In short, the electrons of the atoms in the atomizer can be promoted to higher orbitals for a short amount of time by absorbing a set quantity of energy (i.e. light of a given wavelength). This amount of energy (or wavelength) is specific to a particular electronic transition in a particular element, and in general, each wavelength corresponds to only one element. This gives the technique its elemental selectivity. As the quantity of energy
to the metal [53]. Many modern hollow cathode lamps are selective for several metals.

**Atomizer:** AAS requires that the analyte atoms be in the gas phase. Ions or atoms in a sample must undergo desolvation and vaporization in a high-temperature source such as a flame or graphite furnace. Flame AAS can only analyze solutions, while graphite furnace AAS can accept solutions, slurries, or solid samples. A liquid sample is normally turned into an atomic gas in three steps:

1. **Desolvation (Drying)** – The liquid solvent is evaporated and the dry sample remains.
2. **Vaporization (Ashing)** – The solid sample vaporizes to a gas.
3. **Atomization** – The compounds making up the sample are broken into free atoms.

**Flame:** AAS uses a slot type burner to increase the path length, and therefore to increase the total absorbance (Beer-Lambert law). Sample solutions are usually aspirated with the gas flow into a nebulizing/mixing chamber to form small droplets before entering the flame. The technique typically makes use of a flame to atomize the sample [54], but other atomizers such as a graphite furnace [55] or plasmas (primarily inductively coupled plasmas) are also used [56]. When a flame is used, it is laterally long (usually 10 cm) and not deep. The height of the flame above the burner head can be controlled by adjusting the flow of the fuel mixture. A beam of light passes through this flame at its longest axis (the lateral axis) and hits a detector. The graphite furnace has several advantages over a flame. It is a
much more efficient atomizer than a flame and it can directly accept very small absolute quantities of sample. It also provides a reducing environment for easily oxidizing elements. Samples are placed directly in the graphite furnace and the furnace is electrically heated in several steps to dry the sample, ash organic matter and vaporize the analyte atoms.

**Light separation and detection:** AAS use monochromators and detectors for UV and visible light. The main purpose of the monochromator is to isolate the absorption line from background light due to interferences. Simple dedicated AAS instruments often replace the monochromator with a band pass interference filter. Photomultiplier tubes are the most common detectors for AAS.

**Excitation:** A flame provides a high-temperature source for desolvating and vaporizing a sample to obtain free atoms for spectroscopic analysis. For atomic emission spectroscopy, the flame excites the atoms to higher energy levels.

The narrow bandwidth of hollow cathode lamps makes spectral overlap rare. That is, it is unlikely that an absorption line from one element will overlap with another. Molecular emission is much broader, so it is more likely that some molecular absorption band will overlap with an atomic line. This can result in artificially high absorption and an improperly high calculation for the concentration in the solution. Three methods are typically used to correct for this:

(a). **Zeeman correction:** A magnetic field is used to split the atomic line into two side bands on the basis of Zeeman effect. These side bands are
close enough to the original wavelength to still overlap with molecular bands, but are far enough not to overlap with the atomic bands. The absorption in the presence and absence of a magnetic field can be compared, the difference being the atomic absorption of interest.

(b). **Smith-Hieftje correction**: The hollow cathode lamp is pulsed with high current, causing a larger atom population and self-absorption during the pulses. This self-absorption causes a broadening of the line and a reduction of the line intensity at the original wavelength [57].

(c). **Deuterium lamp correction**: In this case, a separate source (a deuterium lamp) with broad emission is used to measure the background emission. The use of a separate lamp makes this method the least accurate, but its relative simplicity (and the fact that it is the oldest of the three) makes it the most commonly used method.

### 2.4.7. Thin film thickness

Thickness is one of the most important thin film parameter to be characterised, since it plays an important role in the film properties unlike a bulk material. Microelectronic applications generally require the maintenance of precise and reproducible film metrology (i.e., thickness as well as lateral dimensions). Various techniques are available to characterise the film thickness which are basically divided into optical and mechanical methods, and are usually non-destructive but sometimes destructive in nature.

Film thickness may be measured either by in-situ monitoring at the rate of deposition or after the film deposition. The thicknesses of the thin films prepared for the work presented in this thesis were measured by a
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stylus profiler (Dektak 6M). The stylus profiler takes measurements electromechanically by moving the sample beneath a diamond tipped stylus. The high precision stage moves the sample according to a user defined scan length, speed and stylus force. The stylus is mechanically coupled to the core of a linear variable differential transformer (LVDT). The stylus moves over the sample surface. Surface variations cause the stylus to be translated vertically.

Electrical signals corresponding to the stylus movement are produced as the core position of the LVDT changes. The LVDT scales an ac reference signal proportional to the position change, which in turn is conditioned and converted to a digital format through a high precision, integrating, analog-to-digital converter [58]. The film whose thickness has to be measured is deposited with a region masked. This creates a step on the sample surface. Then the thickness of the sample can be measured accurately by measuring the vertical motion of the stylus over the step. The stylus profiler (Dektak 6M) is shown in figure 2.7.
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In modern instruments, the levelling and measurement functions are computer controlled. The vertical stylus movement is digitized and data can be processed to magnify areas of interest and yield best-profile fits. Calibration profiles are available for standardization of measurement.

2.5. References

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