Chapter II

Characterization Techniques

The various characterization techniques used during the course of the present work are discussed in this chapter.

2.1 Introduction

Evaluation of opto-electronic properties of semiconductor nano particles under ambient conditions is the central idea behind this thesis. The characterization of materials in nanoscale can be done using electrons, photons, scanning probes, ions, atoms etc. A wide range of techniques are available in each of these areas and the systematic use of these tools leads to a complete understanding of the system. The information obtained from these techniques can be processed to yield images or spectra which reveal the structural, chemical, geometric or physical details of the materials. While studying the opto-electronic properties of semiconductor nanomaterials synthesized, a range of techniques such as UV-Visible Near Infra Red (UV-vis-NIR) Absorption Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), X-ray Photoemission Spectroscopy (XPS), X-Ray Diffraction (XRD) measurements, Particle Size Measurements, Transmission Electron Microscopy (TEM), Zeta Potential Measurements and Photoluminescence measurements were used. This chapter is devoted to explain the basic principles of the techniques used for characterization.

2.2 UV- Visible Absorption Spectroscopy

Energy absorbed in the UV or visible region causes a change in the electronic excitation of the molecule, and hence results in corresponding change in its ability to absorb light in the UV-visible region of the electromagnetic radiation. This leads to colour transition. The relationship between energy absorbed in an electronic transition and the frequency (υ), wavelength (λ) and wave number ($\bar{v}$) of radiation producing the transition is given as:

$$\Delta E = hv = \ h\frac{c}{\lambda} = h\bar{v}c$$

Where h is Planck's constant

c is the velocity of light

ΔE is Energy absorbed in an electronic transition in a molecule from ground state (lower energy) to excited state (higher energy).

The energy absorbed depends on the energy difference between ground state and excited state; smaller the difference, larger the wavelength of absorption. The principal characteristics of an absorption band are the position and intensity. The position of an absorption band corresponds to the wavelength of radiation whose energy is equal to that required for an electronic transition.

The intensity of absorption depends on two factors:

i) Probability of interaction between the radiation energy and the electronic system.

ii) Difference between the ground state and excited states.

The intensity of absorption is derived from Beer-Lambert's law:

$$A = \varepsilon c l$$

Where A is the measured absorbance

ε is the proportionality constant called absorptivity

l is the path length of the cell

c is the concentration of the analyte

UV-Vis Spectroscopy is a powerful tool for the characterization of semiconductor nano crystals. Optical absorption features of semiconductor nanoparticles can be explained on the basis of excitation of the valence shell electrons to the conduction band, creating an electron-hole pair in the system. The semiconductor nanoparticles display size quantization effects. The dependence of the change in the band gap energy (ΔE_{BG}) in the semiconductor nanoparticles on their size in terms of radius (R) of a spherical particle can be expressed as:

$$\Delta E_{BG} = \frac{h^2\pi^2}{2}\left[\frac{1}{m_e}+\frac{1}{m_h}\right]\frac{1}{R^2} - \frac{1.8\,e^2}{\varepsilon}\cdot\frac{1}{R}$$

Where

m_e and m_h correspond to the effective mass of electron and hole respectively,

ε is the dielectric constant of the semiconductor material [1].

The Quantum size effect on the optical absorption spectra is best known for semiconductor nanoparticles. The decrease in particle size shifts the absorption edge from the infrared to visible region of the electromagnetic spectrum as the band gap energy of the semiconductor increases [2-6].

In the work presented in this thesis UV-Vis absorption spectroscopy has been used to monitor the band gap and absorption characteristics of CdS, Cd MnS, CdYS nanoparticles and Zn, ZnMnS and ZnYS nanoparticles.

The measurements were performed on JASCO-V-570 UV-vis-NIR spectrophotometer operated at a resolution of 1nm [7].

2.3 Transmission Electron Microscopy (TEM)

A beam of accelerated electrons interacts with an object in a conventional TEM. The transmitted electrons are used to create an image of the sample. Scattering occurs when the electron beam interacts with matter. Scattering can be elastic (no energy change) or inelastic (energy change). Elastic scattering can be both coherent and incoherent (with or without phase relationships). Elastic scattering occurring from well-ordered arrangements of atoms as in a crystal; results in coherent scattering, giving spot patterns. This can be in the form of ring in the case of polycrystalline material. Inelastic processes give characteristic absorption or emission, specific to the compound, element or chemical structure.

There are two main mechanisms of contrast in an image. The transmitted and scattered beams can be recombined at the image plane, thus preserving their amplitudes and phases. This results in the phase contrast image of the object. An amplitude contrast image can be obtained by eliminating the diffracted beams. This is achieved by placing suitable apertures below the back focal plane of the objective lens. This image is called the bright field image. Also, all other beams except the particular beam of interest can be excluded. The image using this is called the dark field image.

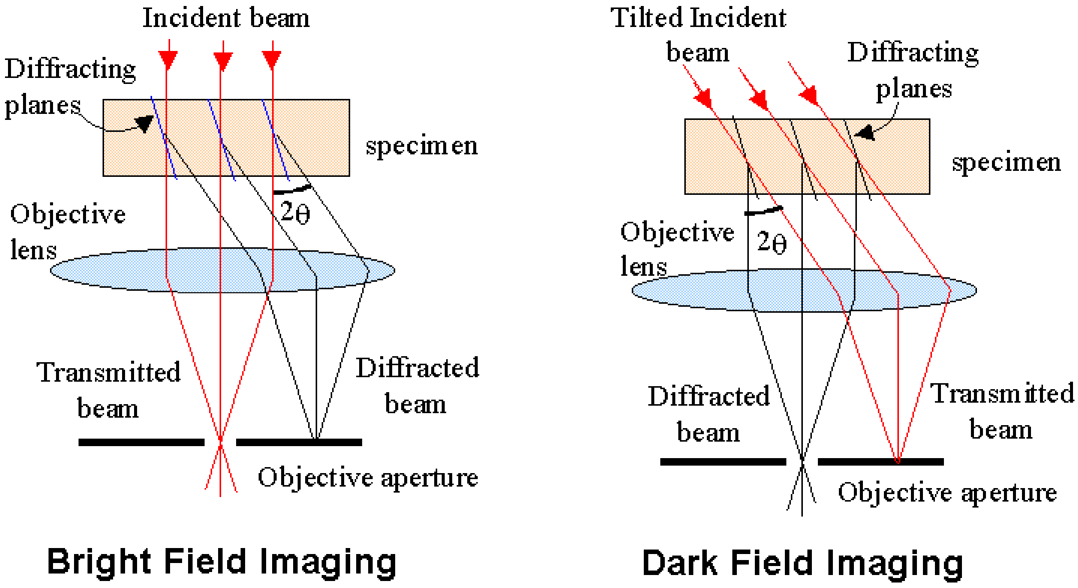

Fig. 2.1 ***Schematic showing bright field imaging and dark field imaging using TEM***

(http://www.mete.metu.edu.tr/pages/tem/TEMtext/TEMtext.html)

Based on the interaction of falling electrons with different elements in the object, differences in light intensity (contrast) are created in the final image, which relates to areas in the object with different scattering potentials. This can be deduced from the Rutherford formula, which describes the deflection potential of an atom:

$$K = \frac{-e.eZ}{r^2}$$

Where K is the deflection potential

e is the electron charge

Z is the positive charge

r is the distance between electron to nucleus

As the atomic number of interacting element increases, their scattering efficiency also increases. In TEM, the great depth of focus provides the high magnification of the sample.

All TEM images presented in the thesis were recorded on a JEOL 1200 EX Instrument at an accelerating voltage of 80kV. Samples were prepared by drop coating the sample on the carbon coated copper grids and allowing the solvent to evaporate.

2.4 X-Ray Diffraction

X-ray corresponds to electromagnetic radiation in the wavelength range is 1Å. The radiation is produced when charged particles are decelerated by metals, thus producing a continuum called Brems Strauhlung radiation. X-rays are generally produced when electrons of several thousands of electron volts are decelerated or stopped by metals.

The crystalline nature and crystal type of the various samples can be identified from their XRD patterns. The XRD samples were made by drop coating the sample on a silica substrate and the diffraction patterns are studied and recorded. When the diffraction pattern is recorded, it shows concentric rings of scattering peaks corresponding to various interplaner spacing in the crystal lattice. The positions and the intensities of peaks are used to identify the underlying crystal structure of the material.

X-rays are electromagnetic radiation with typical photon energies in the range of 100 *e*V – 100 k*e*V. For diffraction applications, only short wavelength X-rays in the range of a few Angstroms to 0.1 Angstroms (1 k*e*V – 120 k*e*V) are used. Since the wavelength of X-rays is comparable to the size of atoms they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials [8]. X-rays primarily interact with electrons in atoms. When X-ray photons collide with electrons, some photons from the incident beam deflect away from their original direction of travel. If the wavelength of these scattered X-rays does not change during this process, this is called elastic scattering (only momentum is transferred in the elastic scattering process, not the energy). These are the X-rays that are measured in diffraction experiments, as the scattered X-rays carry the information about the electron distribution in materials. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference peaks (maxima) with the same symmetry as in the distribution of atoms. Measuring the diffraction pattern therefore allows us to deduce the distribution atoms in the material.

When certain geometric requirements are met, X-rays scattered from a crystalline solid can constructively interfere, producing a diffracted beam. W.L. Bragg in 1912 recognized the following relationship:

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

Where n is the order of diffraction

λ represents the wavelength of X-ray

d is the interplaner spacing and

θ signifies the X-ray scattering angle

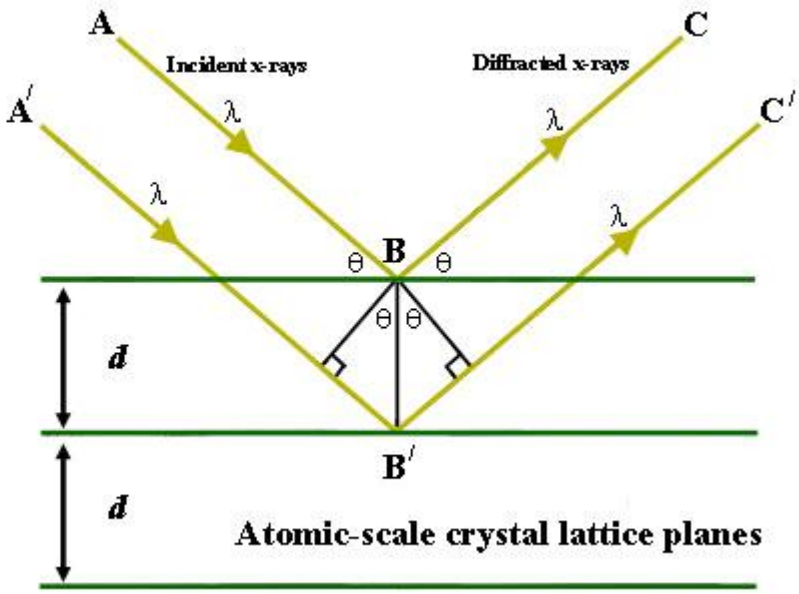

Fig 2.2 ***Bragg's Law reflection***

(*Ref:http://serc.carleton.edu/research_education/geochemsheets/BraggsLaw.html)*

As shown in fig 2.2, consider a crystal with crystal lattice planar distances ***d***. Where the travel path length difference between the ray paths ABC and $A^{/}\ B^{/}\ C^{/}$ is an integer multiple of the wavelength, constructive interference will occur for a combination of that specific wavelength, crystal lattice planar spacing and angle of incidence (θ). Each rational plane of atoms in a crystal will undergo refraction at a single, unique angle.

XRD measurements are carried out using an Xpert PANalytical Pro X-ray Diffractometer instrument operating at 40 *k*V and a current of 30 mA with Cuk_{α} radiation.

2.5 Fourier-Transform Infrared Spectroscopy [FTIR]

The atoms in a molecule do not remain in a fixed relative position and keep vibrating about their mean position. Due to this vibrational motion, if there is a periodic alternation in the dipole moment, such mode of vibrations is infrared (IR) active. The IR region of the electromagnetic spectrum ranges from 100 µm to 1 µm wavelength. The vibrating molecules absorb energy only from those radiations, with which it can coherently interact i.e. the radiations of its own oscillation frequency. This makes each functional group to have specific vibrational frequencies, which is very sensitive to its chemical environment and the neighboring species. The appearance or non-appearance of certain vibrational frequency in IR spectra of any molecule gives valuable information about the structure of that particular molecule. The vibrational frequency is:

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

Where k is the force constant

μ is the reduced mass

The bonds between atoms in the molecule stretch and bend, absorbing infrared energy and creating the infrared spectrum

In FTIR spectroscopy, a mathematical operation known as Fourier transformation converts the time domain signal (intensity Vs time) to the frequency domain signal (intensity Vs frequency) which assists in saving the time required to obtain an IR spectrum [1 sec or less Vs 10 to 15 mins for single scan]. This provides an opportunity to enhance the signal-to-noise (S/N) ratio of IR spectrum by increasing total number of sample scans, since the S/N ratio is proportional to square root of the total number of scans. This explains the term “Fourier transform” used in infrared spectroscopy [9-10]. In FTIR spectroscopy, frequency is conventionally displayed in the form of wave numbers.

All the FTIR measurements of samples were carried out on a Bruker Vertex 70 FTIR spectrophotometer. FTIR spectroscopy has been used in this thesis for obtaining information of the type of nanoparticles and their binding to the surface during the synthesis process. They have been presented as obtained. The baseline correction has not been shown.

2.6 Photoluminescence Measurements

Any form of light emission, other than radiation from a body at high temperature, is said to be luminescence [11]. When luminescence occurs, the system loses energy and if the emission is to be continuous, some form of energy must be supplied from elsewhere. When the external energy supply is by means of the absorption of infrared, visible or ultraviolet light, the emitted light is called photoluminescence.

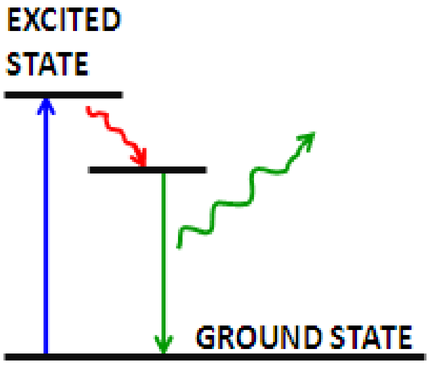

Fig. 2.3 ***Energy diagram showing the principle of luminescence***

A molecule absorbs a high energy photon which excites the molecule to a higher energy state. The molecule then dissipates some of the excess energy due to collisions and emits the remaining energy in the form of photon and returns to the ground state.

To account for the processes of absorption and emission of light, it is necessary to assume that radiant energy can only be absorbed in definite units, or quanta. The energy E, carried by any one quantum is proportional to its frequency of oscillation, that is

$$E = hv = h\,\frac{c}{\lambda}$$

$where\ \upsilon$ is the frequency

λ is the related wavelength

h is Planck's constant

The UV and visible regions of the spectrum and absorption in these regions cause the excitation of the outermost electrons of the molecule. The absorption of light results in the formation of excited molecules which can in turn dissipate their energy by radiation or re-emission. The efficiency with which these processes take place is called the Quantum efficiency and it is defined as the ratio of the number of quanta emitted to the number of quanta absorbed.

At room temperature most molecules occupy the lowest vibrational level of the ground electronic state and on absorption of light they are moved to excited states. Excitation can result in the molecule reaching any of the vibrational sub-levels associated with each electronic state. Since the energy is absorbed as discrete quanta; this should result in a series of distinct absorption bands. The rotational levels associated with each vibrational level increase the number of possible absorption bands.

Having absorbed energy and reached one of the higher vibrational levels of an excited state the molecule rapidly loses it's excess vibrational energy by collision and falls to the lowest vibrational level of the excited state. Also, almost all the molecules occupying an electronic state higher than the second undergo internal conversion and pass from lowest vibrational level of the upper state to the higher vibrational level of the lower excited state which has the same energy from there the molecules again lose energy until the lowest vibrational level of the first excited state is reached from this level. The molecule can return to any of the vibrational levels of the ground state, emitting its energy in the form of fluorescence. If this process takes place for all the molecules that absorbed light, then quantum efficiency of the solution will be maximum unity and for any other route followed, the quantum efficiency will be less than 1.

A plot of emission against wavelength for any given excitation wavelength is known as emission spectrum. If the wavelength of the excitation light is changed and the emission from sample plotted against the wavelength of excited light, the result is the excitation spectrum [12]. The factors that can affect the quantitative accuracy are temperature effects which affect the viscosity of the medium, pH effects, quenching etc.

2.7 X-ray Photoemission Spectroscopy (XPS)

XPS is a highly surface sensitive technique which is used to study the composition and electronic state of the surface region of a sample. XPS is based on well-known photoelectric effect. Photoelectron spectroscopy uses monochromatic source of radiation. In XPS, the photon of energy $h\upsilon$ is absorbed by an atom A in a solid, leading to ionization and emission of core electron. The kinetic energy distribution of the emitted photoelectrons is measured and a photoelectron spectrum is obtained. The overall process of photoionization can be demonstrated as

$$A + h\upsilon = A^{+} + e^{-}$$

Conservation of energy requires that

$$E(A) + h\upsilon = E(A^{+}) + E(e^{-})$$

Since the energy of electron is available solely in the form of kinetic energy (KE), the above expression can be rearranged to get the expression for KE of the photoelectron

$$KE = h\upsilon - [E(A^{+}) - E(A)]$$

$E(A^{+}) - E(A)$ represents the difference in energy between the ionized and neutral atoms, referred to as Binding Energy (BE) of the electron.

$$KE = h\upsilon - BE$$

The BE of electrons in various energy levels in solids are conventionally measured with reference to the Fermi level rather than the vacuum level.

This involves a small correction to the above equation in order to account for the work function of the solid.

$$KE = h\upsilon - BE - \emptyset$$

Using photons of fixed energy $h\upsilon$, if the KE and the work function ($\emptyset$) of the sample are measured, the Binding Energy (BE) of the electron can be calculated. Binding energy being characteristic of atoms, different elements present in the sample can be identified. Electrons travelling through a material have a relatively high probability of experiencing inelastic collisions with locally bound electrons as a result of which they suffer energy loss and contribute to the background of the spectrum rather than a specific peak. However, XPS signals are recorded in the form of peaks only from those photo emitted electrons, which successfully reach the surface without undergoing inelastic collisions. Since the fraction of such electrons decrease significantly with distance, XPS can’t provide information beneath a certain distance from the surface and hence termed as surface sensitive technique.

The exact binding energy of an electron depends not only upon the level from which photoemission is occurring, but also upon the formal oxidation state of the atom and the local chemical and physical environment change in either of these gives rise to small shifts in the peak positions in the spectrum, so called chemical shifts. The ability to discriminate between different oxidation states and chemical environments is one of the major strengths of XPS [13]. Photoelectron peaks are labeled according to the quantum numbers of the levels from which the electron originates. An electron originating from an orbital with principal quantum no: (n), orbital quantum no (l) and spin quantum no s is indicated as nl_{l+s}. For a non-zero orbital quantum no ($l>0$), spin moment is coupled with orbital moment (called L-S coupling) and it has a total momentum ($j = l + ½$) and ($j = l - ½$) (generally $j = l \pm S$), each state being filled with ($2j + 1$) electrons. Hence, most XPS peaks appear in doublets and the intensity ratio of the component is $\frac{l+1}{l}$

XPS spectra with their binding energy were aligned with respect to C1S Band gap Energy of 285 *e*V. The samples were prepared by drop coating the solution on Si Substrate. The chemically distinct components in the core level spectra were resolved by a non-linear least squares filling algorithm after background removal by Shirley method [14].

2.8 Zeta Potential Measurements

Most particles dispersed in an aqueous system will acquire a surface charge, principally either by ionization of surface group or adsorption of charged species. These surface charges modify the distribution of the surrounding ions, resulting in a layer around the particle that is different to the bulk solution. If the particle moves, (under Brownian motion for example) this layer moves as part of the particle. The zeta potential is the potential at the point in this layer where it moves past the bulk solution. This is called the slipping plane. The charge at this plane is sensitive to the concentration and type of ions in solution.

Zeta potential is one of the main forces that mediate inter-particle interactions. Particles with a high zeta potential of the same charge sign either positive or negative will repel each other.

Zeta potential can be high in a positive or a negative sense. $< -30\ mV$ and $> +30\ mV$ are considered to be the minimum requirement of zeta potentials. For molecules and particles that are small enough and of low enough density to remain in suspension, a high zeta potential will confer stability i.e. the solution or dispersion will resist aggregation.

The most important factor that affects zeta potential is pH. Zeta potential is measured by applying an electric field across the dispersion. Particles within the dispersion with zeta potential will migrate toward the electrode of opposite charge with a velocity proportional to the magnitude of the zeta potential.

The frequency shift or phase shift of an incident laser beam caused by these moving particles is measured as particle mobility and this mobility is converted to the zeta potential by entering the dispersant viscosity and the application of the Smolu Chowski or Huckel theories.

The Zeta sizer Nano series uses second generation PALS (Phase Analysis Light Scattering) to measure particle velocity. Phase analysis is 1000 times more sensitive to changes in particle mobility. Malvern Zetasizer Nano ZS is the instrument used for measuring the zeta potentials.

2.9 Particle Size Distribution

Dynamic Light Scattering (DLS) is a technique for measuring the size of particles typically in the sub micron region.

DLS measures Brownian motion and relates this to the size of the particles. Brownian motion is the random movement of particles due to the bombardment by the solvent molecules that surround them. The speed at which the particles are diffusing due to Brownian motion is measured. This can be obtained by measuring the rate at which the intensity of the scattered light fluctuates when detected.

The size of the particles is calculated from the translational diffusion coefficient by using the Stokes - Einstein equation

$$d(H) = \frac{kt}{3\pi\ nD}$$

d(H) - Hydrodynamic diameter

D - Translational diffusion coefficient

k - Boltzmann's constant

t - Absolute Temperature

n - Viscosity

The diameter that is measured in DLS is value that refers to how a particle diffuses within a fluid and so it is referred to as hydrodynamic diameter. The diameter that is obtained by this technique is the diameter of a sphere that has the same translational diffusion coefficient as the particle.

The translational diffusion coefficient depends on the size of the particle "core", surface, structure, concentration and type of ions in the medium.

The rate at which the intensity fluctuations occur due to the phase difference between the scattered light, will depend on the size of the particles. The small particles cause the intensity to fluctuate more rapidly than the larger particles. These intensity fluctuations are measured with correlator that is basically the signal comparator. The time at which the correlation starts to significantly delay is an indication of the mean size of the sample. The steeper the line, the more monodisperse the sample is. The extended the decay becomes, the greater the sample's polydispersity. A correlation function of the scattered intensity is constructed based on the time difference of the correlator.

Size is obtained from the correlation function by using various algorithms.

There are two approaches that can be taken:

1) Fit a single exponential to the correlation function to obtain the mean size (Z-average diameter) and an estimate of the width of the dispersion (polydispersity index).
2) Fit a multiple exponential to the correlation function to obtain the distribution of particle sizes.

The size distribution obtained is a plot of the relative intensity of light scattered by particles in various size classes and is therefore known as an intensity size distribution.

A typical DLS consists of

1) Laser, that provides a light source to illuminate the sample contained in cuvette. For dilute concentrations, most of the laser beam passes through the sample, but some are scattered by the particles within the sample at all angles.
2) A detector is used to measure the scattered light. The intensity of scattered light must be within a specific range for the detector to successfully measure it.
3) An attenuator is used to avoid too much of light being detected and saturating the detector. It is used to reduce the intensity of the laser source and hence reduce the intensity of scattering.
    - For samples that do not scatter much light such as very small particles or samples of low concentration, the amount of scattered light must be increased. In such cases, the attenuator will allow more laser light through to the sample.
    - For samples that scatter more light such as large particles or samples at higher concentration the intensity of scattered light must be decreased.

4) The scattering intensity signal for the detector is passed to a digital signal processing board called a “correlator”. It compares the scattering intensity at successive time intervals to derive the rate at which the intensity is varying.

5) The correlator information is then passed on to a “computer” having zetasizer software which analyses the data and derives size information.

All the particle size distributions have been measured using a Malvern’s Zeta Sizer NanoZS series particle size analyser.

2.10 References

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