Chapter 3

Experimental
Experimental

3.1. Introduction:

In this chapter the electrodeposition method for the synthesis of Nanomaterials is described. The various characterization techniques employed in the present study for the analysis of structure, surface morphology, chemical composition and optical properties are also discussed in this chapter. The field emission configurations used in the present work are described in detail along with vacuum processing and field emission measurements.

3.2. Electrodeposition method:

As discussed in the earlier chapter, Electrodeposition or Electrochemical synthesis, in general, is referred to as preparation of a thin film/coating of desired material on a suitable substrate by means of chemical reaction(s) driven by externally applied electric field. The electrodeposition is carried out under three modes, viz., constant potential (Potentiostatic) or constant current (Galvanostatic) or potential sweep (Cyclic Voltammetry).

3.2.1. Characterization of the electrodeposits:

It should be emphasized that, during electrodeposition the current and/or the potential cannot be controlled simultaneously, and that the electrochemist must choose which experimental variable is to be controlled. Voltammetry refers to those techniques where the potential of an electrode is the controlled variable while the current is the observed variable. Techniques where the opposite is true are termed Galvanostatic methods. Cyclic voltammetry, involves repeatedly sweeping the potential back and forth between the initial and final potentials.
To develop a proper understanding of voltammetry, it is generally a good idea to begin by contrasting it with potentiometry. In potentiometry, the electrochemist assumes a passive role. This means that the solution concentrations are whatever they are, and the electrochemist just measures the working electrode potential. In the more exciting context of voltammetry, things are the other way around, and the electrochemist assumes an active role. By controlling the electrode potential, the electrochemist influences the solution concentrations in the vicinity of the electrode. The potential of the working electrode determines what, if any, redox processes occur at the surface of the electrode. Extremely positive potentials are likely to oxidize analytes while negative potentials are likely to reduce them. In either case, a current flows through the electrode, and the magnitude of this current is usually proportional to solution concentration. Thus, the current provides the analytical signal that can be used as the basis for a calibration curve relating signal to concentration.

This is a good place in the discussion to point out that electrochemical systems are necessarily heterogeneous. All of the interesting chemical and electrochemical events occur at or near the surface of the working electrode. This means that the part of solution very near the electrode is somehow special because it is affected by it. In general, the electrode affects a layer of solution extending just a few micrometers away from the electrode surface. Analyte concentrations in this very small diffusion layer can vary widely from those found in the remaining bulk of the solution. Compared to the overall volume of solution in the cell, the volume of the diffusion layer is minuscule, and concentration changes caused by the electrode in the diffusion layer rarely affect the bulk solution. Faraday's Law provides the link between the observed current and the analyte concentration. In general, higher concentrations mean higher currents. When the electrode potential is perturbed enough from its equilibrium value, the current is limited only by how fast analyte arrives at the electrode surface. In unstirred solutions, the analyte can only reach the electrode by diffusing across the diffusion layer from the bulk solution to the electrode surface. The rate of this diffusion is governed by a concentration gradient, that is, diffusion occurs from a region of high concentration to a region of low concentration and the greater the concentration difference, the faster the diffusion occurs. This means that the current at
an electrode is largest when the gradient in analyte concentration (across the diffusion layer) is greatest.

3.2.2. Experimental Information:

This section is a detailed description of the kinds of equipment needed to perform electroanalytical experiments. The basic equipment needed for electrochemistry is a potentiostat, a recording device, and an electrochemical cell. Everything inside the cell is chemistry, and everything outside of it is electronics. A good workstation will have all of the electrical connections pre-wired and in working order so that person can focus on the chemistry occurring within the cell and the data is being generated by the experiment.

The Potentiostat:

The principle function of a potentiostat is to control potential and measure current. The conventional three-electrode potentiostat is connected to the working, reference, and counter (auxiliary) electrodes immersed in the test solution. It controls the potential of the working electrode with respect to the reference electrode while simultaneously measuring the current flowing between the working electrode and the counter electrode. Note that the potentiostat's internal feedback circuits prevent all but a very small current from flowing between the working and reference electrodes. The more versatile four-electrode potentiostat permits the use of two working electrodes, and for this reason is also known as a bipotentiostat. The potential of each working electrode is maintained independently of the other and with respect to the reference electrode. The current flows between each individual working electrode and the counter electrode. Only an insignificant current flows through the reference electrode.

The Output Device:

The inputs to the potentiostat are the connections to the electrodes in the cell. The outputs from the potentiostat are signal lines reflecting the current and potential of the
working electrode(s). If the potentiostat is interfaced to a computer, these signals are read directly by the controlling software, and experimental data is manipulated, displayed, and stored using the computer.

The Electrochemical Cell:

In its simplest form, the electrochemical cell is a single piece of glassware capable of holding an appropriate volume of a test solution containing one or more electroactive analytes. Immersed in this solution are three electrodes (working, reference, and counter) that are also electrically connected to a potentiostat.

The three necks round bottom flask is a readily available and inexpensive piece of glassware that can be used as an electrochemical cell. These flasks can hold a considerable volume of solution, and the neck openings have large enough diameters that most electrodes will fit through them. Each neck on the flask can be used to mount one of the three electrodes. This configuration is well suited for those experiments where the test solution can be safely exposed to oxygen in the air and where isolation of each electrode in a separate compartment is not required.

The Test Solution:

The test solution inside the electrochemical cell consists of one or more analytes dissolved in a conductive electrolyte solution. The electrolyte solution usually consists of a (relatively) large concentration of an electrochemically inert salt dissolved in an ultra-pure solvent. The purity of the solvent is very important because the sensitivity of most voltammetric techniques is such that even a trace amount of an electroactive contaminant will show up.

To save as much time and money as possible by using a solvent that is inexpensive and readily available, the obvious choice is to use water. Reagent grade acids and bases, diluted to appropriate concentration levels, make excellent solvents for electrochemistry. Similarly, various buffers and inert salt solutions may also be used.
**Electrodes:**

**Choice of Working Electrode:**

The ideal working electrode is a very clean metal surface with a well-defined geometry that is in direct contact with an electrochemical test solution. Working electrodes intended for general purpose work are usually made from a metal that is electrochemically inert over a wide range of potentials. The most widely used metals are platinum, gold, and various forms of carbon. The size and shape of the electrode surface also has an effect on the voltammetric response of the electrode. The overall current observed at an electrode is directly related to its surface area.

**Choice of Reference Electrode:**

The potential of a working electrode in a voltammetry experiment is always controlled with respect to some standard, and that standard is the reference electrode. While the thermodynamic scale of half-reaction potentials found in most textbooks measures electrode potentials against the “standard hydrogen” reference electrode (SHE), in actual practice the SHE is too cumbersome to use. For this reason, a number of other reference electrodes have been developed. Experimental measurements of potential are made against these alternate reference electrodes and then the potentials are “corrected” by simple addition or subtraction and reported against the SHE. One of the most generally available reference electrodes for work in aqueous solutions is the saturated calomel electrode (SCE).

**The Counter Electrode:**

In traditional two electrode cells that have only a working electrode and a reference electrode, current is necessarily forced to flow through the reference electrode whenever a measurement is made. If enough current flows through a reference electrode, its internal chemical composition may be significantly altered, causing its potential to drift away from the expected standard value. For this and other
reasons, it is desirable to make electrochemical measurements without current flowing through the reference electrode. Modern three and four electrode potentiostats use a feedback circuit to prevent this from happening, but this feedback circuit requires that an additional counter electrode be introduced into the electrochemical cell. This counter electrode provides an alternate route for the current to follow, so that only a very small current flows through the reference electrode. The counter electrode can be made from just about any material using any desired electrode geometry. Design choices are usually based on finding a material that is chemically inert in the particular test solution being studied, and it is generally a good idea for the counter electrode to have a large surface area. In most cases, a coil of platinum wire is used, but stainless steel, copper or aluminium wire may work in non-corrosive solutions where metal cation interference is not a concern. The schematic diagram of the electrochemical set-up is shown in Figure (3.1).

Figure (3.1): Schematic diagram of Electrochemical Analyzer set-up.
3.2.3. Experimental Details:

A computer controlled electrochemical analyzer (Model – 1100A Series, CH Instrument, USA) was employed to maintain the cathodic polarization condition at a potential of -1.4 V versus the SCE. In order to perform the deposition at the desired temperature, first the cell temperature was increased slowly using an oil bath and once stable desired temperature was reached, the electrodes were immersed into the electrolyte. Prior to electrodeposition, the Zinc foil and platinum sheet were degreased and cleaned to remove the contaminants, if any, present on the surface. The electrolyte was constantly stirred during deposition experiments. The electrodeposition set-up is shown in the Figure (3.2). At least three specimens were synthesized under identical experimental conditions and characterized by various analytical techniques in order to check the reproducibility and repeatability of the results.

Figure (3.2): Photograph of Electrodeposition set-up.
3.3. Characterization techniques:

In the previous chapter, methods for the synthesis of nanomaterials (especially for ZnO) were presented. Along with the synthesis processes, the nanomaterials need to be characterized to assess their physical and chemical properties. A large number of techniques can be employed for nanomaterials characterization. Some of the most common characterization techniques in nanotechnology such as XRD, SEM, EDS, TEM, HRTEM, SAED, XPS, PL and FEM will be presented in this chapter.

3.3.1. X-ray Diffraction (XRD):

XRD involves monitoring the diffraction of X-rays after they interact with the sample. It is a crystallographic technique used for identifying and quantifying various crystalline phases present in solid materials and powders. Using XRD the crystal structure as well as the size of grains and nanoparticles can be determined. When X-rays are made incident on a crystalline sample, a proportion of them are diffracted to produce a pattern. From such a pattern the crystal phases can be identified by comparison to those of internationally recognized databases (such as Powder Diffraction File, International Center for Diffraction Data – JCPDS).

XRD is one of the most utilized techniques for determining the structure of inorganic and organic materials [1]. It is also widely used for studying nanostructured thin films and nanoparticles. However, the materials must have ordered structure, and it cannot be used directly to study amorphous materials. Another inherent limitation of XRD is that mixtures of phases that have low symmetry are difficult to differentiate because of the larger number of diffraction peaks.

In crystallography, the solid to be characterized by XRD has a space lattice with an ordered three-dimensional distribution (cubic, rhombic, etc.) of atoms. These atoms form a series of parallel planes separated by a distance $d$, which varies according to the nature of the material. For any crystal, planes have their own specific $d$-spacing. When a monochromatic X-ray beam with wavelength $\lambda$ is irradiated onto a crystalline material with spacing $d$, at an angle $\theta$, diffraction occurs only when the distance traveled by the rays reflected from successive planes differs by an integer number $n$ of
wavelengths to produce constructive interference. Such constructive interference patterns only occur when incident angles fulfill the Bragg condition such that:

\[ n\lambda = 2dsin\theta \]  

(3.1)

By varying the angle \( \theta \), the Bragg Law condition is satisfied for different \( d \)-spacings in polycrystalline materials. Plotting the angular positions versus intensities produces a diffraction pattern, which is characteristic of the sample. When a mixture of different phases is present, the resultant diffractogram is a superposition of the individual patterns [2].

In a typical XRD pattern, the diffracted intensities are plotted versus the detector angle \( 2\theta \). Each peak is then assigned a label indicating the spacing of a crystal plane. Bragg’s law states the condition for sharp diffraction peaks arising from crystals which are perfectly ordered. Actual diffraction peaks have a finite width resulting from imperfections, either the irradiation source or the sample, in addition to the natural broadening. A useful phenomenon is that as crystallite dimensions enter the nanoscale the peaks broaden with decreasing crystal size. It is known that the widths of the diffraction peaks allow determination of the crystallite size. Practically, the size of crystallites can be determined using variants of the Scherrer equation.

\[ t = \frac{K\lambda}{B\cos\theta} \]  

(3.2)

where \( t \) is the thickness of the crystal, \( K \) is a constant which depends on the crystallite shape, and \( B \) is the full width at half maximum of the broadened peak. If a Gaussian function is used to describe the broadened peak, then the constant \( K \) is equal to 0.89. The Scherrer equation is derived from Bragg’s law and may be used to determine crystallite sizes if the crystals are smaller than 1000 Å. XRD has many practical uses for nanotechnology. Not only does it allow for different phases to be identified, it can also be used to monitor the growth and formation of nanosized crystallites by examining the broadening of peaks in the XRD pattern.

The XRD analysis of the all specimens was performed using X-ray diffractometer (Model-D8 Advance, Bruker AXS) using Cu k\( \alpha \) (\( \lambda = 1.54 \text{ Å} \)) X-ray source.
3.3.2. Electron Microscopy:

Electron microscopes have played an integral role in the rapid advancements of nanotechnology and nanoscience. Electron microscopes utilize a highly energetic beam of electrons that interacts with a material. From the interaction, information regarding topography, chemical composition, morphology and crystallographic structure can be obtained. Electron microscopes are suitable for the characterization of both organic and inorganic materials. However, as they employ high-energy electron beams, prolonged exposure to the beam may cause certain materials, particularly organic polymers and biological materials, to be damaged, deformed, or destroyed. Furthermore, electron microscopes generally operate at high vacuum and consequently not suitable for samples that contain a liquid component or outgas.

Electron microscopes have a much better resolution than their optical counterparts because of the interaction of an electron’s matter wave with the sample. From Bragg’s law, the minimum separation, \( d_{\text{min}} \), which can be resolved by any microscope, is given by:

\[
d_{\text{min}} = \frac{\lambda}{2\sin \theta}
\]  

(3.3)

The resolution can be improved by using shorter wavelengths. The wavelength associated with an electron is given by the de Broglie relation:

\[
\lambda = \frac{\hbar}{p} = \frac{\hbar}{\sqrt{2m_eE_k}}
\]  

(3.4)

Where, \( m_e \) the electron mass, \( E_k \) is its kinetic energy, and \( \hbar \) is Planck’s constant. The electrons in the microscope obtain their kinetic energy by an applied electric potential in the order of kilo or even mega volts. Depending on the kinetic energy, a typical range of wavelengths can be between \( 1 - 0.005 \) Å, which is much smaller than that of visible light (4000 - 7000 Å) used in optical microscopes, resulting in far better resolution. As a consequence, nano-scale features, not observable with optical microscopes, can be observed.
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Figure (3.3): Schematic of various interactions when high energy electron beam strikes the specimen.

Figure (3.4): Electron penetration in specimen.
When a beam of high energy electrons strikes a solid object, it causes number
interactions which in turn produce different kinds of emissions which contain
information on the atomic, crystallographic and topographic nature of the region from
where they originate. Different emissions along with electron penetration are
illustrated in Figures (3.3) and (3.4), respectively.

3.3.3. Scanning Electron Microscope (SEM):

The SEM is perhaps the most routinely utilized instruments for the
characterization of nanomaterials. With an SEM it is possible to obtain secondary
electron images of organic and inorganic materials with nanoscale resolution,
allowing topographical and morphological studies to be carried out, by scanning an
electron probe across a surface and monitoring the secondary electrons emitted.
Compositional analysis of a material may also be obtained by monitoring X-rays
produced by the electron-specimen interaction. Thus detailed maps of elemental
distribution can be produced.

A schematic diagram of an SEM is shown in Figure (3.5). The electron beam is
emitted from a heated filament, which is commonly made from lanthanum hexaboride
(LaB₆) or tungsten. The filament is heated by applying a voltage, which causes
electrons to be emitted. Alternatively, electrons can be emitted via field emission
(FE). The electrons are accelerated towards the sample by applying an electric
potential. This resulting electron beam is focused by a condenser lens, which projects
the image of the source onto the condenser aperture. It is then focused by an objective
lens and raster-scanned over the sample by scanning coils. This is achieved by varying
the voltage produced by the scan generator on the scan coils that are energized,
creating a magnetic field, which deflects the beam back and forth in a controlled
pattern [3].
When the primary electrons hit the sample, they give away part of their energy to the electrons in the sample, resulting in emission of secondary electrons. These secondary electrons have lower energies (around 20 eV) and are collected by a suitable collector (an Everhart-Thornley detector). The output of the detector is amplified and used to build up the image. Their intensity is displayed versus the position of the primary beam on the sample. The samples placed in the SEM must be either conducting or covered with a thin metal layer in order to avoid electric charging. Scanning takes place at low pressures, so that the electrons are not scattered by gas molecules inside the chamber. Furthermore, with an SEM it is possible to
obtain images from comparatively large area of the sample. Also, SEM can monitor the formation and growth of thin films and nanostructures.

In addition to the secondary electrons, there are also high-energy electrons, originating in the electron beam (producing X-rays), that are backscattered from the specimen interaction volume. These electrons may be used to detect contrast between areas with different chemical compositions. SEM are often coupled with X-ray analyzers e.g. energy dispersive X-ray spectrometer (EDS or EDAX).

The SEM analysis was carried out using JEOL, JSM-6360A for all specimens. The microscope was operated at an accelerating voltage of 20 kV and filament current of ~60 μA.

### 3.3.4. Transmission Electron Microscope (TEM):

In TEM, a beam of focused high energy electrons is transmitted through a thin sample to reveal information about its morphology, crystallography, particle size distribution, and its elemental composition. It is capable of providing atomic-resolution lattice images, as well as giving chemical information at a spatial resolution of 1 nm or better. Because the unique physical and chemical properties of nanomaterials not only depend on their composition, but also on their structures, TEM provides a means for characterizing and understanding such structures. TEM is unique as it can be used to focus on a single nanoparticle in a sample, and directly identify and quantify its chemical and electronic structure. Perhaps the most important application of TEM is the atomic-resolution real-space imaging of nanoparticles. A TEM operates in a similar manner to a slide projector. As the electron beam passes through the sample, only certain parts of it are transmitted, making an amplitude contrast image. The image passes through a magnifying lens and is then projected onto a phosphor screen or a charge coupled device (CCD), which allows for quantitative data processing. Information may also be obtained from backscattered and secondary electrons, as well as emitted photons. A wide variety of materials can be characterized with a TEM, including metals, minerals, ceramics, semiconductors, and polymers. Because electrons must be transmitted through the material this requires that the sample be appropriately thin. The electron gun is a pin shaped cathode that is
typically made from materials such as LaB₆. Heating this cathode by applying a large current produces a stream of almost monochromatic electrons that travel down a long column after being accelerated by a large voltage. Increasing this voltage increases the kinetic energy of the electrons and hence decreases their wavelength. The smaller the electron beam wavelength the higher the resolution, although the quality of the lens systems is the limiting factor. The condenser lenses focus the beam to a small and coherent cylinder while the condenser aperture removes electrons scattered at large angles. The beam strikes the specimen on the sample holder, and the majority is transmitted, focused by the objective lens, after which it passes through the intermediate and projector lenses and enlarged. Eventually by striking a phosphor or CCD surface it forms an image.

Electrons can traverse the sample without any interaction (unscattered electrons) or can be scattered, elastically or inelastically, on their way (scattered electrons). There are two modes of operation for TEM, forming electron diffractions and imaging. Elastically scattered electrons do not lose energy during the interaction. Thus, all incident electrons scattered by the same atomic plane will be deflected under the same angle. The electrons can be collected using magnetic lenses to form a pattern of spots, the electron diffraction pattern, which is projected onto a viewing screen. By readjusting the lens system, it is possible to form images by TEM. There are two main imaging modes. In bright-field imaging, the image is formed exclusively by the unscattered electrons. Contrast in these images is due entirely to thickness and density variations in the sample. Dark-field imaging, on the other hand, uses a single diffracted beam to form the image. This causes all regions of the specimen, which possess a different crystal structure or orientation than the sample zone producing the diffracted beam, to appear dark. A simplified two modes of operation for TEM setup are shown in Figure (3.6).

Thus, the TEM has the capability to create both electron microscope images (information in real space) and diffraction patterns (information in reciprocal space) for the same region by adjusting the strength of the magnetic lenses. By inserting a selected area aperture and using parallel incident beam illumination, a selected area electron diffraction pattern (SAED) from an area as small as several hundreds to a few nm in diameter is obtained.
Crystal structures can also be investigated by high resolution transmission electron microscopy (HRTEM) where the images are formed due to differences in phase of electron waves scattered through a thin specimen. The emergence of HRTEM has allowed the direct reconstruction of Bragg differential electron beams to create interference patterns, which in favorable cases of simple projected electrons, give a representation of the underlying crystallographic diffraction grating.

Figure (3.6): Schematic diagram of ray paths in a reference transmission electron microscope. (a) High resolution high magnification imaging mode. (b) Selected area diffraction mode.
The TEM analysis was carried out using Technai, TM G2 F30, at National Chemical Laboratory, Pune, India, and Philips, EM-CM-12, at Banares Hindu University, India. For HRTEM analysis, FEI, Tecnai 20 G2, at Banares Hindu University, India was used. We employed simple method to prepare the specimens for TEM observations. The sample was scratched and the flakes thus obtained were sonicated in acetone. A drop of acetone containing the ZnO nanostructures was placed on the TEM grid.

Clearly, the TEM can to provide a wide range of information from nanostructured materials, including diffraction patterns, lattice constants and particle sizes. Furthermore, the fact that an individual nanoparticle can be selected and characterized individually makes TEM one of the most powerful characterization techniques in nanotechnology.

3.3.5. Photoluminescence (PL):

Photoluminescence (PL) is a nondestructive and contact less spectroscopic method of probing the electronic structures of materials. Light is shined in the samples, which is absorbed by the sample and upon de-excitation, light is emitted by the sample known as photo-emission, and this mechanism is generally known as photo-luminescence i.e, light is incident upon the sample and the emitted light is collected. As shown in Figure (3.7) the electrons and holes thermalize by emitting phonons and reach lower lying energies. Electrons and holes recombine, producing photons which are then detected.

Electrons and holes can recombine through a number of processes: i) In band to-band recombination electrons and holes recombine directly from the conduction and valence bands; ii) Recombination after formation of “free” excitons; and iii) Excitons can be trapped by impurities such as donors and acceptors creating transitions from donor-bound-excitons or acceptor-bound-excitons [4].
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Figure (3.7): A schematic showing how electrons and holes scatter from high energies to thermalize. Various energies for excitonic and other features are shown.

If the carriers recombine radiatively, the energy of the emitted light can be analyzed to determine the energy of the defect or impurity level. Levels which lie near the conduction or valence band edges, are more likely to participate in radiative recombination. Deep levels are involved in non-radiative recombination by providing a stop-over for electrons making their way between the conduction and valence band by emitting phonons.
Schematic of the instrument used for luminescence experiment is illustrated in Figure (3.8).

![Schematic of photoluminescence instrument](image)

**Figure (3.8): Schematic of photoluminescence instrument.**

It contains a source of radiation. High pressure dc Xe arc lamp is used for this purpose. The xenon lamp emits an intense and relatively stable continuum from 300 to 1100 nm. A primary filter or excitation monochromator in the excitation path selects specific wavelengths or bands and directs them to the sample to be analyzed.

PL spectroscopy is used to characterize variety of material parameters. It is a selective and extremely sensitive probe of discrete electronic states. Features in the emission spectrum are used to identify properties of surface, interface and impurity levels. PL intensity gives the measure of relative rates of radiative and non radiative recombination. Variation of PL intensity with external parameters like temperature and pressure can be used to study further the underlying electronic states and bands. The resultant luminescence is isolated by secondary filter or emission monochromator and finally recorded by a detector. Generally photomultiplier tube (PMT) is used to detect the luminescence. We have carried out PL studies using a Perkin Elmer-LS-55. The exciting wavelength was ~ 325 nm.
3.3.6. X-ray Photoelectron Spectroscopy (XPS):

X-ray photoelectron spectroscopy (XPS) or more commonly known as Electron Spectroscopy for Chemical Analysis (ESCA) is a powerful technique to analyze surface of specimens. XPS can quantify the chemical and electronic states of the elements within the first few atomic layers of a surface. It can be used to identify elements, their chemical bonds, and hence the chemical composition and empirical formulae. Two main things one can get from the data of XPS are (1) the energies of the molecular or atomic orbitals and their identification and (2) the shift in the energy of a core electron of a given element as a function of the chemical nature of the surrounding.

The XPS is based on the photoelectric effect, in which X-rays cause photoelectrons to be ejected from a surface. In an XPS experiment, the source of the X-rays is generally the Ka emission from magnesium (Ka = 1256.6 eV) or aluminum (Kα = 1486.6 eV). The X-rays strike the sample surface and interact with the atomic electrons in the sample, primarily via photon absorption (Figure 3.9) [5, 6].

Figure (3.9): Electronic orbits showing the ejection of a photoelectron after absorption of a photon.
The focused X-ray beam which impinges on the sample has energy of approximately 1.5 keV while the reflected photoelectrons have smaller energies. The reflected photoelectrons only escape from the very top surface of the sample (generally not more than 10 nm). The kinetic energy and number of the ejected photoelectrons is plotted as a spectrum of their binding energies. The acquired spectrum is compared with spectra from known databases. The peak positions and shapes correspond to the material's electronic configuration, and therefore elements and compounds show their own unique characteristic peaks.

As XPS involves monitoring emitted photoelectrons, the experiments must be conducted under ultra high vacuum and therefore the sample should not outgas. Furthermore, exposure to the X-ray beam can damage certain materials, mainly organic molecules and polymers, and they may degrade during the measurement. XPS experiments are limited to just a few Ångstroms beneath the surface, despite the incoming X-rays being able to penetrate microns into the surface. This is because the ejected electrons must travel through the sample and yet retain enough energy to reach and excite the detector. Only electrons that are emitted by atoms near the surface have a chance to leave the sample. When the XPS instrument is combined with ion beam sputtering, atomic layers can be continuously removed from the surface. After sputtering, the XPS may be performed once again on these layers, and as a result compositional depth profiles can be obtained down to a few micrometers [7]. As the incident X-rays can penetrate deep into the atom, they can eject electrons from several energy levels. The incident X-rays have energy of $h \nu$ and can pass on energy to the ejected electron according to the following equation:

$$KE = h \nu - BE - \phi$$

where,

$KE =$ kinetic energy of the emitted photoelectrons  
$h \nu =$ energy of the incident photon  
$BE =$ binding energy of the atomic orbital from which the electron originates  
$\phi =$ spectrometer work function
Probability of interaction of electrons with matter is far greater than that of photons. These are the electrons which are important in the analysis and are detected. The other electrons which lose part of their energy form background in the spectrum. If an electron of an inner atomic shell is ejected from the atom, then an electron from the outer shell will fill the empty space it leaves behind. Two things may then happen, either a photon (whose energy is equal to the difference between the two energy levels) will be emitted, or the energy is transferred to another outer electron that is then emitted. This emitted outer electron is called an Auger electron, and consequently Auger Electron Spectroscopy (AES) can be used to analyze these emitted electrons. Both these processes are schematically summarized in Figure (3.10).

![Figure (3.10): The photoelectric and Auger processes in (A) XPS and (B) AES.](image-url)
Analysis of the samples was carried out using a Microtech ESCA-LAB 3000 spectrometer manufactured by VG Scientific, UK. The spectrometer is equipped with a twin anode X-ray source. One can switch between Al ($K_\alpha$, $h\nu = 1486.6$ eV) and Mg ($K_\alpha$, $h\nu = 1256.6$ eV) anodes. A concentric hemispherical analyzer was used to analyze the emitted photoelectrons.

Relative concentration of elements present in the sample can be determined using the XPS data. Area under the curve and atomic sensitivity factor for each element present in the sample is used to determine the concentration.

Number of photoelectrons per second for a particular peak is given by

$$I = nf\sigma\theta y\lambda AT$$  \hspace{1cm} (3.6)

Where

- $n$ = number of atoms of a particular element per cm$^3$
- $f$ = X-ray flux in photons/cm$^3$ – sec
- $\sigma$ = photoelectric cross section for the atomic orbital of interest
- $\theta$ = angular efficiency factor for the instrumental arrangement
- $y$ = efficiency in the photoelectric process for the formation of photoelectrons
- $\lambda$ = mean free path of the photoelectrons
- $A$ = area of the sample from which photoelectrons are detected
- $T$ = detection efficiency

Therefore from equation (3.5) can be written as

$$n = \frac{I}{f\sigma\theta y\lambda AT}$$  \hspace{1cm} (3.7)

By putting $f\sigma\theta y\lambda AT = S$ = atomic sensitivity factor

$$n = \frac{I}{S}$$  \hspace{1cm} (3.8)
3.3.7. Field electron emission microscopy:

3.3.7.1. Parallel plate geometry:

In close proximity (C-P) or parallel plate diode configuration, the cathode is in the form of thin film, held in front of an anode (a metal sheet or a semitransparent phosphor screen). The conducting anode screen is prepared by coating a cathodoluminescent phosphor on SnO₂ coated glass plate. The typical separation between cathode and anode in C-P configuration varies from 50 μm or a few mm. Either the emitter cathode or the anode screen is attached to linear motion drive, to facilitate variation in the cathode-anode separation. The field emission study of thin film cathodes or nanostructure arrays is carried out in close proximity configuration.

In close proximity configuration, the electric field, generally termed as average electric field is given by \( E = \frac{V}{d} \) where \( d \) is the separation between cathode and anode, \( V \) is voltage applied to cathode. In case of thin film emitter consisting of anisotropic structures (like nanowires, nanoneedles, nanobelts, etc.), the local electric field at the apex of these structures is by \( E_{local} = \frac{\beta V}{d} \) [9], where \( \beta \) is the field enhancement factor or local field conversion factor. Usually, for a single nanowire or a nanoneedle, the field enhancement factor \( \beta \) is defined as \( \beta = \frac{h}{r} \), where \( h \) is length of the wire and \( r \) is the wire diameter. Recently, according to Filip model [10] the local electric field at the apex of the emitter is given \( E_{local} = s \frac{V}{r} + (1-s) \frac{V}{d} \), where \( r \) is the radius of the emitter, \( s \) is a parameter describing the degree of the screening effect (\( s = 0 \), for densely arranged emitters and 1 for a single emitter). The ability of an emitter to amplify the applied electric field is

\[
\beta = 1 + s \left( \frac{d}{r} - 1 \right) = 1 + s \frac{d}{r} \quad (3.9)
\]

The schematic diagram of the close proximity configuration and photograph of the all metal field emission microscope (FEM) system (containing the close proximity arrangement) are shown in Figure (3.11).
Figure (3.11): (A) Instrument used for field electron emission studies, (B) Schematic diagram of the planar diode configuration assembly.
The as-synthesized and annealed thin film specimens on zinc foil (substrate) are used as field emitter cathodes in planar diode configuration. The sample is mounted on a stainless-steel stub (Ø ~ 6 mm) using silver paste, for proper ohmic contact. A phosphor screen held parallel to the cathode, used as an anode and is mounted on a linear motion drive. The linear motion drive facilitates variation in cathode-anode separation. The cathode-anode assembly is introduced in a metal chamber, which is mounted on the ultra high vacuum (UHV) system.

3.3.7.2. Vacuum processing:

After fixing the specimen on the stainless-steel stub, it was mounted onto an all metal UHV system. This UHV system consists of a rotary pump for roughing and backing, turbo molecular pump, a sputter ion pump (SIP), which can be isolated from the rotary and turbo molecular pumps by an isolation valve and a titanium sublimation pump (TSP) with liquid nitrogen jacket. The system is equipped with ion gauge for pressure measurement. After checking the system for leaks at rough vacuum, the system is baked at 150 °C for 8-10 hours. Before transferring the system to SIP, the ion gauge and TSP are degassed thoroughly when system is hot enough. Further, the system is transferred to SIP to maintain the vacuum. After cooling, the system pressure of $1 \times 10^{-7}$ mbar is observed. Further the TSP with a LN$_2$ jacket was fired to attend ultimate vacuum better than $1 \times 10^{-8}$ mbar.

3.3.7.3. Field emission measurements:

For the field emission current-voltage (I-V) and current-time (I-t) measurements, the experimental setup consists of Spellman high voltage power supply (± 40 kV), Keithely 485 Picoammeter and the planar diode configuration assembly. After making proper electrical connections (as depicted in the schematic of Figure 3.11(B)), the voltage applied to the cathode (emitter, specimen) is increased very carefully and the resultant emission current is measured on the electrometer. The turn on voltage is usually defined as the value of the applied voltage required to draw emission current of 1 nA. The I-V measurement deals with recording the values of applied voltage and
the corresponding field emission current, which can be spanned over a wide range from 1 nA to several hundred μA. In general, the turn-on field value strongly depends upon the tip morphology, size, density, crystallinity and alignment of the 1D nanostructures [11].

Further, increasing the cathode voltage carefully the field emission image was observed on the screen. The photographs are recorded with digital camera. At least three set of measurements were taken to check the reproducibility of the experimental results. The current versus voltage (I-V) data is used to plot current density versus applied field curve and Fowler-Nordheim (F-N) plot. Nature of the F-N plot verifies the quantum mechanical tunneling phenomenon of field electron emission. The slope of the F-N plot in linear region is used to determine the value of field enhancement factor ($\beta$). In each case, the emission current density ($J$) is obtained by dividing the emission current ($I$) value by the total area of the emitter surface ($A$), i.e. $J = I/A$.

The emission current stability is a decisive property for application of the cathode in field emission based devices. The current stability is recorded for preset value of current at fixed voltage. For the field emission current stability (I-t) measurements, by applying some fixed voltage to the cathode an emission current is set to initial value (of several nA to several μA, as per the specimen) and the emission current values are recorded after an interval of 10 or more seconds. For long term stability measurement values of the field emission currents are recorded for more than three hours duration. After taking proper precautions, the I-V and I-t measurements were performed at base pressure of $1 \times 10^{-8}$ mbar with cathode at room temperature.

3.3.7.4. Error determination:

The error involved in the current measurement has major contribution from the experimental conditions such as vacuum, adsorption/desorption process on the surface, effect of ion bombardment etc. This leads to instability in the emission current values. The error in emission current is estimated by recording several (at least three) different sets of I-V measurement. The average value of current density has been used for further J-E and F-N analysis. For this analysis the standard deviation from the average current density value is calculated for all applied electric fields. The
typical behaviour of J-E and F-N plots are shown in Figure (3.12). The error bars in J-E plot show root mean square deviation of current from the mean value. The corresponding errors in F-N plot are also represented.

Figure (3.12): Field emission J-E and F-N plot with error bars.
3.3.8. Photoconductivity measurements:

Photoconductivity occurs when carriers are optically excited from non-conductive to conducting states. It is an indirect measure of the recombination and does not distinguish between radiative and non-radiative mechanism. The measurement of photoconductivity was performed using a home made set up at room temperature and at atmospheric pressure. A specimen of dimension 1 cm x 1 cm on zinc substrate was taken for measurement. This specimen was loaded to a sample holder specially designed and the contacts were made with silver paste. A voltage of 20 V DC was applied to the electrodes and the current was measured with an electrometer (Keithley, model 6514). After this dark current measurement, the specimen was illuminated by a tungsten halogen lamp, with an intensity 100 mW/cm², which was calibrated using a standard c-Si solar cell. The measurements were taken about 10 second after the light was put ON. The Figure (3.13) shows the schematic of electrode geometry used for the conductivity measurement.

![Diagram of conductivity measurement](image)

**Figure (3.13): Schematic of conductivity measurement**

The values of dark conductivity and photoconductivity were calculated from the relation,

\[ \text{Photosensitivity} = \frac{I_{\text{Dark}}}{I_{\text{Photo}}} \]  \hspace{1cm} (3.10)

Where, \( I_{\text{Dark}} \) and \( I_{\text{Photo}} \) are Dark current and Photo current in amperes, respectively.
References: