Chapter II
Various synthesis routes and growth mechanism

The present chapter elaborates on various routes used for the synthesis of 1D nanowires and 2D nanosheets. The various techniques applied for the characterization of the synthesized products are described in brief. The thermal evaporation and the hydrothermal techniques adopted for the synthesis of the 1D and the 2D nanostructures respectively, are discussed in detail. The field emission setup is described along with vacuum processing. The actual experimentation of recording the FE data is also discussed. The chapter also includes a detail study of the growth mechanisms relevant to the growth of 1D and 2D nanostructures.

2.1. Synthesis of nanomaterials: different routes

Nanomaterials are generally synthesized by two approaches: the top-down and the bottom-up approach. The top-down approach involves cutting down the bulk material to smaller dimensions until the nano-dimension is approached, whereas in bottom-up approach, the basic individual entities (like single atom or molecule) are assembled to obtain the nanoforms. The preparation methods can be classified as chemical or physical methods.

2.1.1. Chemical synthesis route

The Chemical synthesis route\(^1\)\(^-\)\(^2\) uses the chemical properties of the material to undergo certain chemical reactions, such as reduction or decomposition, so as to etch down the bulk material or bound the entities to obtain the nanomaterials. Certain medium and external energy is required to carry out the reaction. The energy provided externally can be of the different form such as, thermal, photon (solar/UV/IR), sonochemical (ultrasonic agitation), electrical (electrochemical), irradiation etc. Sometimes along with the precursors certain catalysts or surfactants are added to initiate and control the reaction. The process is then called *catalyst assisted synthesis*. The pH of the medium plays a vital role in the synthesis process. The major drawback of this route is the uncontrolled growth of the nanostructures. Skillfully optimized parameters have to be adopted to obtain the desired morphology of the nanomaterials and also the reproducibility. The different synthesis routes are discussed below briefly:

(a) Colloidal method: The method involves mixing of chemicals together to obtain a colloidal suspension of the nanoparticles (i.e. insoluble precipitate). A surfactant is used to control the size of the nanoparticles.
(b) Sol-gel method: In this method the sol i.e. a colloidal solution is processed to form a gel-like network which confines the size of the nanoparticles. The method benefits from obtaining uniform morphology of the nanoparticles.

(c) Electrodeposition method: The method induces a chemical reaction into an aqueous electrolyte by applying voltage across electrodes immersed in the electrolyte. The potential difference between the electrodes ionizes the electrolyte leading to the deposition of ions on one of the electrode. The reaction is carried out in an electrolytic cell. The cell consists of generally three electrodes; working, counter and reference electrode. The working electrode is one on which the nanostructure gets deposited. The counter electrode, also called as auxiliary electrode, balances the current observed at the working electrode while the deposition process is occurring. The reference electrode is not directly involved in the deposition process but provides a stable preset potential. The potential at other electrodes are measured with reference to this electrode.

(d) Solvothermal method: The synthesis is carried out in a high temperature non-aqueous solution kept in an autoclave. Generally metal precursors are mixed in a solvent and the temperature of the solution is maintained above the critical temperature so as to increase the solubility of the precursors.

2.1.2. Physical synthesis route

The Physical synthesis routes3–6 involve mechanical crushing, milling or the synthesis based on heat treatment to the bulk particles. Certain physical synthesis methods are discussed below.

(a) Mechanical grinding (milling): As the name suggests, the bulk material is mechanically grinded to break it down to nanoforms. There is energy transfer from the grinder to the bulk (which is mostly in powder form) which causes the breakage. This technique is cost effective but suffers due to contamination.

(b) Physical Vapor Deposition (PVD): PVD process basically involves vaporization of a solid (mostly in powder form). The vapors formed are transported by the carrier gas, under low pressure condition which then condenses on the substrate.

(c) Solid state synthesis or solid state reaction: As the name suggests, solids are physically mixed together and the mixture is heated to elevated temperature to obtain the nanoforms.
2.2. Synthesis of 1D SnO$_2$ nanowires: synthesis methods

2.2.1. Solvothermal route

The solvothermal synthesis route involves synthesis of various nanomaterials like semiconductors, ceramics, polymers etc. by mixing the precursors in a non-aqueous medium and at high pressure and temperature ranging from 100-1000°C. The process of mixing facilitates the reaction among the precursors at the elevated temperature and pressure. The method provides uniformity in shape and size and also the crystallinity of the metal oxide nanostructure. Anandam and Rajendran report a simple, cheap and relatively safe method for synthesis of tetragonal shaped SnO$_2$ nanocrystals. The authors report that with increase in synthesis temperature, the size of the nanocrystalite is observed to increase. Highly crystalline SnO$_2$ nanoparticles were synthesized at the water-oil interface. The oxidation of Sn$^{2+}$ was carried out at the interface which leads to formation of tin oxide nanoform. $^8$ The method was also used to obtain a composite of tin oxide and graphene. $^9$

2.2.2. Template assisted method

Patterning the growth and assembling the nanostructure is beneficial for device fabrication. In order to obtain a well aligned and oriented growth of 1D nanostructure, the substrate can be pre-processed by using various templates. The growth of 1D structure can be controlled for its diameter, inter-spacing and number density by choosing the appropriate template. In case of field emission investigations, the patterned growth of the nanostructure array reduces the screening effect. As a routine procedure, certain hard template such as anodic aluminium oxide (AAO) is used to obtain a patterned growth. The growth of nanostructures is obtained through the template pores. Nanotubes and nanorods of SnO$_2$ were synthesized using AAO template by Q. Li et. al. $^{10}$ They proposed a single step growth process using hydrothermal route. Later on the template was dissolved using aqueous solution of NaOH. A simple infiltration technique was employed using AAO template to obtain SnO$_2$ nannotubes. Synthesis of SnO$_2$ nanotubes by electrochemical deposition technique using polycarbonate membranes was reported by M Lai et. al.$^{11}$ Lithography is also a strong technique for patterning the substrate. Chavan et. al. have used a photographic plate to pattern the Au/Si substrate for the growth of CdS nanowires. $^{12}$

2.2.3. Electrochemical deposition method

Electrochemical deposition is one of the prominent methods used for obtaining large scale deposition of SnO$_2$ nanowires/rods etc. The concentration of the individual component forming the solution, applied potential, duration etc. decide over the final
quality of the film achieved. K R Prasad and N Miura in 2004 demonstrated for the first time the use of electrochemically deposited SnO$_2$ nanostructures for supercapacitor applications. The authors have used four electrode cell. Electrochemical deposition technique was used for large-scale synthesis of SnO$_2$ nanowires using AAO template.\textsuperscript{14,15}

2.2.4. Hydrothermal method

Hydrothermal method of synthesis involves formation of nanostructures at lower temperatures than that required in calcinations processes. It was shown by X. Zu et al.\textsuperscript{16} that citric acid assisted hydrothermal method can be adopted to obtain a controlled growth of the SnO$_2$ nanoparticles. An early report in 2002 by Y. D. Li\textsuperscript{17} and co-workers have shown the formation of nearly spherical nanoparticles of SnO$_2$. The authors have termed the synthesis process as a hydrolytic process. Hydrothermally synthesized SnO$_2$ nanoparticles of small dimensions (~ 3nm) are proposed as a good sensor material for alcohol.\textsuperscript{18} Doping SnO$_2$ with various dopants is also possible via hydrothermal synthesis route.\textsuperscript{19} Various morphologies of SnO$_2$ are reported to have been synthesized by this route.\textsuperscript{20–23} The morphology variation can be obtained by varying the deposition time. X Peng et. al.\textsuperscript{21} have synthesized 1D nanorods, 2D nanosheets and 3D nanospheres with the same primary source of tin just by varying the concentration of polyethylene glycol (PEG), CO(NH)$_2$ and Na$_2$SnO$_3$. The authors have also proposed the plausible growth mechanism.

2.2.5. Thermal evaporation (vapour transport) method

Thermal evaporation is a well known and most widely used method for the synthesis of tin oxide 1D nanostructures. The morphology of the synthesized product is governed by various parameters like, temperature, duration etc. A number of reports on synthesis of undoped and doped SnO$_2$ nanostructures and its various composites using the thermal evaporation method are found in literature.\textsuperscript{24–33} The synthesis of SnO$_2$ nanostructure by the thermal evaporation technique dates back in 1990s.\textsuperscript{33}

The thermal evaporation method is used in the present work to obtain the doped and undoped 1D SnO$_2$ nanostructures. The thermal evaporation method is discussed in details in further section.
Thermal evaporation synthesis method is based on the vaporization of powders (precursor) at a high-temperature zone, and their subsequent deposition at a low-temperature zone, which results in the formation of specific nanostructures at specific temperature zones. The thermal evaporation system consists of an iron shielded tube furnace loaded with a quartz tube. The tube has windings of nichrome (alloy of nickel and chromium) wire on it. The windings are dense at the centre of the quartz tube and become rare towards the ends. The windings are connected to the AC mains which passes current through it. The tube is heated following the Joule’s heating law. The space between the iron shield and the tube is packed by glass wool which provides thermal insulation. The open ends of the quartz tube are connected to the inlet and the outlet of the carrier gas using quartz couplers, respectively. The furnace is provided by a thermocouple just above the centre of the quartz tube, to monitor the temperature. The furnace has a Portable-Integral-Derivative (PID) controller to programme the furnace.

The desired source material (usually in the form of powder) is placed at the centre of an alumina or quartz boat that is inserted into a horizontal tube furnace, where the temperature and evaporation time are controlled. At the set reaction temperature, the source material evaporates. The vapors formed are transported by a carrier gas. The carrier gas can be an inert gas such as argon or any other gas like nitrogen, oxygen etc. as per the requirement of the reaction. Sometimes a mixture of argon gas and small quantity of oxygen gas is used to facilitate the oxidation reaction in the furnace. The vapors carried, finally get deposited onto either the substrate or the inner walls of the alumina/quartz boat.
Throughout the experiment the carrier gas flow is kept constant. The schematic of the thermal evaporation system used for the synthesis of SnO$_2$ nanoforms is shown in Fig. 2.1. and the actual photograph of the furnace is shown in Fig. 2.2.

![Thermal Evaporation System Schematic]

Fig. 2.2. Actual photograph of the tube furnace

### 2.3.1. Choice of substrate

For field emission investigations, the substrate on which the nanostructures are deposited need to be electrically conducting. Most of the researchers have used silicon as a substrate for the deposition of various nanostructures. Stainless steel foil is also used by some researchers. In the present work p-type Si (111) is used as the substrate. As Si is easily adaptable in monolithic circuits, the deposited nanostructures can find direct applications in device fabrication. However, for the growth of nanowires on Si, a catalyst layer in the form of thin gold film is used. Gold, as a catalyst has following properties:

1) zero oxide formation (It is not an oxygen hungry material!),
2) easy to deposit (1064C),
3) chemically inert and unaffected by air, moisture etc.

The gold film provides a control on the growth of the nanowires. The thickness of the catalyst layer plays a vital role in deciding the size and shape of the nanostructures. The optimization of the Au film thickness was obtained after a series of pilot experiments.

The details of the actual experimental parameters are given in Chapter 3.
2.4. Hydrothermal synthesis: furnace construction and working

The hydrothermal synthesis route involves synthesis of a crystal in certain *aqueous* medium, at high temperature and high pressure conditions. The method is similar to the solvothermal route described before, only difference being the use of aqueous medium. The synthesis via this route is carried out mostly around 300°C, as the ionic product for water has a maximum value in the range 250-300°C. The ionic product for water (\(k_w\)) is an equilibrium constant for an aqueous base reaction where water simultaneously acts as both base and acid.\(^{34}\) Controlled size and morphology of the nanostructures can be achieved by this route. The choice of solvent and pH of the solution have dominant control over the overall growth of the nanostructures. The solubility and the reactivity of the reactants are quite different at high temperature and high pressure. The high pressure condition is favourable for the crystallization of the product. The reaction parameters, like temperature, duration, concentration of the solvents have to be tuned to maintain simultaneously high nucleation rate and desired size distribution.

The hydrothermal reaction is carried out in a Teflon lined stainless steel autoclave in which the reacting aqueous solution is kept. The autoclave is tightly fixed with stainless steel lid which helps in developing the desired pressure. The schematic of the experimental set-up is shown in Fig. 2.3. The autoclave is placed in a furnace which is provided with a thermocouple to monitor the temperature and a PID to set the reaction parameters.

![Fig. 2.3. Schematic of the furnace and the autoclave used in hydrothermal synthesis method](image-url)
Thus, the advantages of the hydrothermal method can be summarized as below:

1. The synthesized product can be obtained in the form of anhydrous, crystalline or amorphous powders depending on the processing parameters. With insertion of suitable substrate, the direct growth of the nanostructures on the substrate can be achieved.

2. Particle size and shape of the nanostructures can be controlled and reproducibility can be established.

3. The chemical composition, stoichiometry etc. can be controlled.

4. In most of the cases, the as-synthesized powders do not require post treatments like calcination or milling.

The only disadvantage of the hydrothermal route is the inability to observe the growth process.

The actual photograph of the system used is shown in Fig. 2.4.

![SS autoclave with Teflon lining](image)

**Fig. 2.4. Actual photograph of the furnace used for hydrothermal method**

The growth of 1D nanowires and 2D nanosheets is governed by vapour-liquid-solid and Ostwald’s ripening mechanism, respectively. Both the mechanisms are discussed in details in the following sub topics.

### 2.5. Synthesis of nanosheets: a brief report

The hydrothermal synthesis is the most widely adopted route for obtaining the 2D nanostructure. Several reports on synthesis of 2D SnS$_2$ nanosheets or nanosheets-like structures are found in literature.$^{35-36}$ Also, solvothermal$^{37-38}$, solution based chemical
39 and chemical vapour deposition\textsuperscript{40} techniques along with chemical exfoliation\textsuperscript{42,43,44} methods are used to obtain pristine and various composites of SnS\textsubscript{2} and WS\textsubscript{2} 2D structures. In the present work, hydrothermal synthesis method is followed to obtain 2D nanosheets.

2.6. Vapor-Solid-Liquid (VLS mechanism)

The Vapour-Liquid-Solid, VLS mechanism is proposed for the growth of 1D nanowires. The mechanism is catalyst-assisted as existence of the catalyst layer on the substrate provides the nucleation sites for the 1D growth of the nanostructure. VLS mechanism was proposed for the first time by Wagner and Ellis in 1964.\textsuperscript{45} The mechanism basically involves three steps:

1) Formation of liquid droplet of the catalyst layer on the substrate.
2) Introduction of the precursor vapours which are absorbed by the catalyst liquid drop.
3) Supersaturation of the catalyst drop, nucleation and growth of the 1D nanostructure.

Thus, the catalyst plays a vital role in the growth mechanism. The catalyst must fulfil the following requirements:

1) it must be chemically inert.
2) it must be in liquid form at the growth temperature.
3) the catalyst liquid drop must not vaporize or shrink in size during the growth process so that the growth does not terminate.

The angle of contact made by the catalyst drop with the substrate decides over the growth area. The mechanism can be illustrated taking an example of synthesis of SnO\textsubscript{2} nanowires which is performed in the present work. For the synthesis of SnO\textsubscript{2} nanowires certain amount of Sn powder (precursor) is placed in a ceramic boat. The Au coated Si wafer (substrate) is kept at elevated distance from the precursor. The boat is then inserted into the quartz tube which is mounted in the furnace. Argon is allowed to flow through the tube. The required temperature and the duration of reaction are set. Specific rate of Ar gas flow is maintained throughout the experiment. As the desired temperature is reached, the precursor vaporizes. Simultaneously, the catalyst forms a liquid phase. The vapours, carried away by the carrier gas, are absorbed by the catalyst liquid drop, thus forming a eutectic mixture. The drop when supersaturates with the Sn vapours results in it’s precipitation. Eventually, the precipitate column grows along the vertical direction,
forming a 1D nanowire. The schematic representation of the VLS mechanism is shown in Fig. 2.5

![Schematic of VLS mechanism](image)

The observation of the gold nanoparticles at the apex of the nanowire marks the signature of VLS growth mechanism. The diameter of the nanowire is observed to be dependent on the diameter of the catalyst drop formed.

### 2.7. Ostwald’s ripening mechanism

The process of dissolution of inhomogeneous crystals in a solution followed by re-deposition of homogeneous crystals on larger surfaces is termed as Ostwald’s ripening process. The process was first described by Wilhelm Ostwald in 1896. The dissolution of the solute leads to supersaturation of the solution. On supersaturation, the smaller dissolved crystals tend to condense on certain larger surfaces.

![Schematic of Ostwald’s ripening mechanism](image)

Thus, the process of nucleation and growth is initiated. The mechanism is schematically shown in Fig. 2.6. The size of the crystal is a function of concentration of the solute, duration of reaction, reaction temperature and the various combinations of the
above mentioned factors. The growth of 2D nanosheets follow the Ostwald’s ripening mechanism.

2.8. Characterization techniques

The synthesized nanostructures are characterized prior to field emission investigations for their structural analysis. The various characterization techniques used are discussed in brief.

2.8.1. X-ray diffraction (XRD)

X-ray diffraction analysis reveals information about the crystallographic structure and physical properties of materials which are in the form of powders and thin films. It is a non-destructive technique. The X-rays have wavelengths of the order of a few angstroms which is also the typical range for inter-atomic distances in crystalline solids. Therefore, X-rays can be diffracted from the periodic arrangement of atoms, which is characteristic of crystalline materials. The diffraction of the X-rays being elastic in nature, there is conservation of the energy before and after the diffraction. The necessary condition for X-ray diffraction is given by the Bragg’s law which is given as,

\[ 2d \sin \theta = n \lambda, \]  

where \( d \) is the inter-planer distance, \( n \) is the order of diffraction from the lattice plane and has an integral value, \( \lambda \) is wavelength and \( \theta \) is the angle of incidence made at the diffraction plane by the incident ray. The analysis of the XRD peaks provides information about the crystal structure and the inter-plane spacing.

In the present work X-ray diffraction analysis of the as-synthesized product containing various nanostructures was performed using X-ray diffractometer (Model-D8 Advance, Bruker AXS) using CuKα \( (\lambda = 1.5402 \ \text{Å}) \) X-ray source available in the department of Physics, SPPU.

2.8.2. Scanning electron microscope (SEM) and Field electron scanning electron microscope (FESEM)

The morphological characterization of the synthesized nanostructures was done by observing them under Scanning Electron Microscope (SEM). The electron probe is made to scan the surface of the material under study. The secondary electron image obtained is used for morphological and topographical studies. When the primary electrons are incident
on the specimen, some part of their energy is imparted to the specimen resulting in
generation of secondary electrons. These secondary electrons have low energies (~ 20eV).
They are collected by a collector (Everhart-Thornley detector). The output of the detector
is amplified and the image then is build up. The entire process of electron emission from
the electron gun and scanning of the specimen takes place in high vacuum condition (~10^{-6}
mbar) which helps in minimizing the scattering of the electrons by the ambient gas
molecules inside the chamber.

Along with the secondary electrons, X-rays are also generated. The X-rays are
backscattered from the specimen interaction volume. These X-rays are used to detect
contrast between areas with different chemical compositions. Hence, elemental
composition of the specimen can be done with the help the Energy Dispersive Spectroscopy, EDS. Many times the SEM is coupled with EDS for analysis. In the present
work SEM analysis was carried out using JEOL, JSM-6360A. The microscope was
operated at an accelerating voltage of ~ 20 kV and filament current of ~ 60 µA with a
resolution of 5 nm and magnification in the range of 8X to 300000X.

The FESEM is another powerful technique adopted for the structural analysis. The
basic working principle is the same as that of SEM apart from the field emission based
electron source; hence the name FESEM. As discussed in Chapter I, the FE electrons are
highly monochromatic and coherent, also the energy spread of the e-beam being less (FE ~
0.3 eV and for thermionic emission ~ 1-3 eV). This helps in obtaining less electrostatically
distorted image. For the present work, the FESEM facility at CSIR National Chemical
Laboratory, Pashan Pune is used (FEI ESEM QUANTA 200 3D having resolution of 1.0
nm and the maximum magnification upto 1,000,000X).

2.8.3. Transmission Electron Microscope (TEM)

The unique physical and chemical properties of nanomaterials are due to their
nanoscale dimensions. So a detail structural analysis of the nanomaterials is required.
Transmission electron microscopy (TEM) is a powerful technique for analysis of
microchemistry, crystal structure and the defect structure of the crystalline material. The
atomic scale resolution is obtained with High Resolution TEM, HRTEM. The HRTEM
provides an image of atomic arrangement of the specimen. The conventional microscope is
equipped with an electron gun which works on thermionic emission process. The emitted
electrons are made to traverse through the specimen. The transmitted electrons, which
interact with the specimen, are used for image construction.
The TEM chamber is evacuated to $10^{-6}$ to $10^{-8}$ mbar pressure. Most of the common types of TEM are capable of accelerating the thermionically emitted electrons through a selected potential difference in the range of 40-200 kV. The appropriate electron energy depends upon the nature of the specimen and the information required. Below the electron gun there are two or more condenser lenses. The condenser lenses de-magnify the beam emitted by the gun and control its diameter (about 1 to 50 µm) and thus the intensity of illumination. As a result parallel and coherent beam of electrons are transmitted through the specimen. The objective lens is so strong that the specimen sits within its pole pieces. The role of objective lens is to form the first intermediate image and diffraction pattern. An essential feature of the objective system is the aperture. The objective aperture clearly defines the angular range of scattered electrons which can travel further down the column and contribute to the image formation. The first image produced by the objective lens usually has a magnification of 50-100 times. This is further magnified by a series of intermediate and projector lenses and is finally projected onto the fluorescent screen. By using three or four lenses further magnification is possible to obtain the final image on the screen.

The crystallographic analysis of the specimen is also possible along with recording of the TEM image. This is achieved through Selected Area Electron Diffraction (SAED) pattern. The electrons are diffracted by the crystal planes of the specimen. The diffracted electrons form a spot-like pattern, depending upon the crystal structure, on the screen.

In this work the TEM and SAED analysis is done by using Tecnai, G2 20 U-Twin (FEI, Netherlands) instrument having resolution of 5nm and magnification upto 100X.

2.8.4. Photoluminescence (PL)

Photoluminescence (PL) spectroscopy is an effective method to evaluate the nature of transitions and defects in materials. PL is a non-destructive and contact less spectroscopic method. In a typical process light illuminated on the specimen is absorbed by the material (specimen) and the electrons are excited. Eventually, the electrons de-excite, emitting energy in the range of visible light. This mechanism is generally known as photoluminescence. As depicted in Fig. 2.7. the corresponding processes are summarized which take place on illumination of light.

Electrons and holes can recombine through a number of processes:

i. electron hole pair photo-generation,
ii. recombination through recombination centres,
iii. band-to-band (excitons) recombination,
iv. hole emission processes, which are shown in the Fig. 2.7.

![Diagram of possible processes in Photoluminescence](image)

**Fig. 2.7. Schematic illustration of the possible processes occurring in Photoluminescence**

The radiative recombination can be analyzed to determine the energy of the defect/impurity level. The energy levels close to the conduction band or the valance band edges are more prone to participate in the above process. 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 photons.

For recording PL spectrum, in the present work, high pressure Xenon (Xe) arc lamp is used. The Xe 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 specimen to be analysed. The PL study in this work was done using a Perkin-Elmer-LS-55. The excitation wavelength was ~ 325 nm.

### 2.8.5. Raman Spectroscopy

Raman spectroscopy which is a non destructive technique is used to study the vibrational, rotational and other lower frequency modes of a molecule. The Raman peaks obtained in the spectrum are fingerprints for the molecule identification. The spectroscopy is based on scattering of light by matter which is capable of probing the structure of gases, liquids, and solids, both amorphous and crystalline. The specimen is irradiated with a monochromatic beam of photons (mostly LASERs are used as they are highly monochromatic, as sources of radiation). The laser of suitable wavelength depending on the specimen is used for irradiation. If the specimen is transparent to the incident
radiations, most of the radiations are transmitted. A small fraction of the incident radiation is elastically scattered (known as Rayleigh) while another small fraction is inelastically (Raman) scattered. In the inelastic scattering event, the energy of the incident photons can decrease or increase by Stokes or anti-Stokes. The Stokes and anti-Stoke processes are important for understanding the Raman spectroscopy and can be explained as follows,

a) Stoke process: If the final vibrational state of molecule is more energetic than the initial state, then emitted photon will be shifted to a low frequency (with respect to Rayleigh process) for conserving the energy of system. This shift in frequency is known as Stoke Shift.

b) Anti-Stoke process: If the final vibrational state of molecule is less energetic than the initial state then emitted photon will be shifted to a high frequency (with respect to Rayleigh process). This shift in frequency is known as anti-Stoke shift.

Overall, the change in polarizability determines the Raman scattering intensity. The inelastically scattered radiation is collected and is then plotted as a function of its wave number of irradiation. The wave number is proportional to its momentum (in units of reciprocal centimeters). Each peak in the spectrum corresponds to one or more vibrational modes of the solid and the modes are termed as Raman active modes. Raman spectroscopy is popularly used for the analysis of carbon based materials.

2.8.6. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR characterization technique is a widely used for the analysis of vibrational modes of a molecule when subjected to IR exposure. The technique is also useful for detecting the bonding between the atoms in a molecule. When the specimen is exposed to IR radiations, those frequencies which match with natural vibration frequencies of molecule are absorbed. This increases the amplitude of vibrational motion of the bonds in the molecules. Since every bond has different natural frequency of vibration, no two molecules of different structure have exactly the same IR absorption pattern or IR spectrum. In the FTIR spectrophotometer, a mirror placed at a 45° splits the incident beam. The mirror separates beam as one is undeflected while other is oriented to 90°. The beam oriented to 90° returns from stationary mirror back to beam splitter. The undeflected beam also returns back to the beam splitter from a moving mirror. Motion of mirror causes the variation in the path length of beams. When two beams meet at beam splitter they have different path length and they form interferograms. The beams are passed through sample which absorbs the wavelengths that are found in infrared region. Modified interferogram
signal reaches to detector which contains information about the amount of energy that was absorbed at every wavelength. The computer compares the spectrum with standard data. The FTIR spectrum can also be employed to detect the bonding between the base structure and the doped atom.

In the present work, the doped and undoped SnO$_2$ nanowires were characterized by Fourier Transform Infrared Spectrometer (Model – JASCO, 6100). The spectrum is recorded in the range of 400-1800 cm$^{-1}$ for each specimen.

2.9. Field emission studies: setup and configuration

This section describes the experimental setup and the vacuum processing required for the Field emission investigations.

2.9.1. Experimental setup and vacuum processing

The field emission studies of the specimens are carried out in an in-house constructed vacuum chamber. Two types of experimental setups are available, namely, *All metal chamber* and *All metal chamber with load-lock assembly*. The initial vacuum processing required to obtain the final UHV conditions for both the setups is almost similar.

![All metal system](image)

*Fig. 2.8. All metal system*

An ultra high vacuum (UHV) condition (~10$^{-8}$mbar) is required for the FE investigations. The specimen subjected to field emission study is initially mounted on a stub (copper stub in case of *All metal chamber* and stainless steel in case of *load-lock*
assembly). The specimen is pasted on the stub with the help of vacuum compatible conducting silver paste. In case of powder specimen conductive carbon tape can be also be used. The stub is then mounted in the vacuum chamber. The all metal system UHV chamber consists of a rotary backed turbo molecular pump. The two pumps are operated to attain a pressure of $\sim 10^{-6}$ mbar. The system is then checked for any leak and is fixed if found any. The chamber is baked for $\sim 12$ hours at 200C. Post baking the system is connected to sputter-ion pump (SIP), which is isolated from the rotary and turbo molecular pump by an isolation valve. The titanium sublimation pump with a liquid nitrogen jacket is also connected to the chamber to attain a final pressure of $\sim 10^{-8}$ mbar. The baking of the system extracts the adsorbed molecules in the inner walls of the chamber. The chamber is equipped with a hot cathode ion gauge (Bayard and Alpert Ionization gauge) for pressure measurement.

The All metal chamber with the load lock assembly is also equipped with the above mentioned vacuum pumps. The load-lock system consists of two chambers, the working chamber and the load-lock chamber. The specimen is mounted in the system at the load-lock chamber which is then transferred to the working chamber via the transfer rod. Thus, the two chambers are isolated by a gate valve. The working chamber is maintained between the vacuum ranges of $10^{-6}$ to $10^{-8}$ mbar. The isolation of the two chambers reduces the vacuum processing time. The load-lock assembly is shown in Fig. 2.9.

![Fig. 2.9. All metal chamber with load-lock assembly](image)
2.9.2. Parallel plate configuration of anode and cathode

The field emission investigation of the specimen is carried out in a close proximity or parallel plate diode configuration. In this configuration the emitter acts as cathode while the phosphor coated conducting glass held in front of cathode acts as anode. The conducting anode is prepared by coating cathodoluminescent phosphor on SnO$_2$ coated glass plate. The typical separation between anode and cathode can be varied from 20µm to few mm using a linear motion drive attached to the cathode. The diode configuration arrangement can be schematically represented as shown in Fig. 2.8 (inset). The parallel plate arrangement for multiple tip emitters and single tip emitter is shown in Fig. 2.10.

The cathode is provided by a high voltage power supply (Spellman, USA) while the anode is grounded via a 100 kΩ resistance. The voltage drop across the anode and cathode is measured by a digital multimeter (Rishabh, 14S series) connected across the resistance. For such kind of arrangement the average electric field, $E$ is given as the ratio of applied voltage, $V$ and the inter-electrode distance, $d$. Thus, $E = V/d$.

Fig. 2.10. Parallel plate diode configuration for (a) multiple tip emitters and (b) configuration for a single tip

In case of single tip emitter, the electron emission features strongly depend upon the geometry of the tip apex. Fig. 2.11 represents various geometries of a tip. It is obvious that the tip with blunt apex will emit electrons at higher applied electric field. Thus, the emission current ($I$) will depend on radius of curvature of the tip apex, work function of the emitter and the emitter number density.
2.9.3. Error determination

The error involved in the current measurement has major contribution from the experimental conditions such as base vacuum, adsorption/desorption process on the surface, effect of ion bombardment etc. leading to instabilities in the emission current values. The error in the 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 FN 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 plot (of specimen: SnO₂ nanowires) is shown in Figure 2.12. The error bars in the J-E plot show root mean square deviation of current from the mean value.

![Fig. 2.11. Various geometries of emitter tips](image)

![Fig. 2.12. Field emission J-E plot with error bars](image)

In the preceding chapters the average values of the plotted entities are taken into consideration. So for the J-E and FN plots the error bars will not be shown henceforth.
The next chapter describes the actual FE experiments carried out on doped and undoped SnO$_2$ nanowires. The results of the characterization techniques performed are analysed.
References


