CHAPTER 2

Synthesis Routes and used Experimental Tools and Techniques

In this chapter, the different synthesis and growth techniques used for the development of oxide DMS NSTs (NPs, NWs and NRs) are discussed in details. A simple physical doping technique as ball-milling method, a chemical doping method with controlled variation by solvothermal reaction route using a Teflon coated stainless steel autoclave and a vapor deposition method by using an in–house developed thermal vapor deposition (TVD) system is presented in detail. Several standard analytical and spectroscopic techniques used for the different characterizations are presented in this chapter and brief information about the various experimental techniques and tools used for this thesis work are discussed.

2.1 Oxide DMS Nanostructures Grown by a Ball Milling Technique

Zn$_{1-x}$TM$_x$O, Ti$_{1-x}$TM$_x$O$_2$ (x = 0, 0.03, to 0.10, weight percentage) NSTs are synthesized by a ball milling technique in a mechanical ball milling machine (Retsch, PM 100, shown in Figure 2-1) with the use of zirconium oxide ball and a zirconium oxide vial under atmospheric pressure and temperature to avoid any contamination from the ball and vial. Zirconium oxide balls having diameter of 5 mm are used in this experiment.

The PM 100 planetary ball mill is a benchtop unit designed to grind soft, fibrous and brittle materials. The mill develops extremely high centrifugal forces resulting in energy input that is up to 50% higher than in other planetary ball mills. It has a single grinding station for grinding jars with a nominal volume of 12 to 500 ml. The unit can store up to 10 combinations of speed, grinding time and interval settings for use with
repetitive grinding tasks. All relevant data can be entered or called up via the multi-
language graphic menu interface with one-button operation. Extraction fan exchanges
air at a per hour rate more than 20 times the chamber volume. The single station mill
features a counterweight that can be adjusted on an inclined guide rail. The counterweight
allows for compensation when using the different size grinding jars with differing centers
of gravity and avoiding oscillations of the machine.

The various synthesis conditions and parameters which have been carefully controlled in
order to achieve uniform doping with single phase nature of the material without any
contamination are as follows:

1) TM (Co, Ni, Mn) type, concentration (3-8%) of doping, initial particle size of precursor
materials.

2) Ball to powder weight ratio (10:1), milling time variation (2-15 h).

3) Adjustment of the counterweight on the guide rail to avoid oscillations, rpm speed of
milling (300-400 rpm).

Figure 2-1 Planetary Ball mill Machine and set up
2.2 Zn_{1-x}(TM)_xO DMS Nanostructures Grown by Chemical Synthesis: Solvothermal and Hydrothermal Method

The Solvothermal or hydrothermal method is a simple and environment friendly chemical reaction technique which does not require the use of organic solvents or additional processing of the product. The synthesis takes place in an autoclave, where the mixture of reagents and solvent is heated gradually in temperature range of 100–300 °C, for several hours (2-20 h). As a result of heating followed by cooling, crystal nuclei are formed, which then grow. This process has many advantages, including the possibility of carrying out the synthesis at low temperatures, the diverse shapes and dimensions of the resulting crystals depending on the composition of the starting mixture and the process temperature and pressure, the high degree of crystallinity of the product, and the high purity of the material obtained.\textsuperscript{201,202} The chemical reaction is carried out in a stainless steel autoclave with teflon lining in the reaction flask. The photograph of the autoclave used in this study and a flow chart of synthesis method are shown in Figure 2-2.

Synthesis Details:

Here we use zinc acetate dihydrate (Zn (Ac)\(_2\), 2H\(_2\)O) and cobalt acetate tetra hydrate (Co (Ac)\(_2\),4H\(_2\)O), nickel acetate tetra (Ni (Ac)\(_2\),4H\(_2\)O) of analytic grade and sodium hydroxide (NaOH) pellets (Merck) for the synthesis of undoped and doped ZnO NSTs. Distilled deionized (DI) water and ethanol are used during all the experiments. In a typical synthesis, (Zn(Ac)\(_2\), 2H\(_2\)O) and (TM(Ac)\(_2\), 4H\(_2\)O) of different molar percentages are mixed with 50 ml DI water with continuous stirring for 1 h. In the two-step synthesis process, the pre-stirring step is essential for the growth of TM doped ZnO nanorods, as it yields an intermediate product of Zn(OH)\(_2\), which serves as a reservoir and slowly releases Zn\(^{2+}\) ions to allow the nucleation and growth for ZnO. Next the solution mixture is transferred into Teflon-lined autoclave (Berghof, BR-100) of 100 ml capacity. Then 25 ml NaOH solution (1 M) is drop wise added with increasing temperature up to 90 °C in few steps, under continuous stirring. We carefully observe that this kind of slow reaction with drop caste addition of NaOH have tendency for the TM ions to insert inside the ZnO matrix and distribute quite well. While just mixing the precipitates all together and heating have chances to produce TM related secondary phases also it might lead to
irregular shaped nanocrystals. Next the chamber is closed and the mixture is heated at different temperatures (120–150) C for 5-20h. and then cooled down to RT naturally. The precipitates are collected, alternately washed with deionized water several times till the pH~7 is reached and finally dried in room temperature. The final products with colors from light green to deep green are obtained with the increasing doping concentration.

\[
\text{Zn(CH}_3\text{COO)}_2 + \text{NaOH} \rightarrow \text{Zn(OH)}_2 + 2\text{CHCOONa}
\]

\[
\text{Zn(OH)}_2 \rightarrow \text{ZnO + H}_2\text{O}
\]

**Figure 2-2** Photograph of the Teflon-lined autoclave autoclave with hot plate heater. And a flow chart of Solvothermal synthesis process.
2.3 Zn_{1-x}(TM)_xO DMSs Nanowires /Nanorods Grown by Thermal Vapor Deposition

Vapor phase growth for the growth of 1D ZnO NSTs by using TVD system is a widely used technique. For our present study we have developed a TVD system in our laboratory. Photograph and schematic diagram of this system is shown in Figure 2-3. It consists of a horizontal muffle furnace, a closed cylindrical quartz/alumina tube with vacuum accessories and gas flow option through a mass flow controller. One side (inlet) of the quartz/alumina tube is connected to the Ar gas cylinder through a mass flow controller (MFC) and other side (outlet) is connected to the rotary pump as exhaust side. The whole system is placed inside the split type horizontal muffle furnace. The chamber pressure is monitored using a pirani gauge connected to the tube at the exhaust side. We achieved a chamber base pressure of $16\times10^{-3}$ mbar without any flow of Ar gas. During the flow of Ar gas, i.e. during the deposition the chamber pressure is fixed to a desired value using a gate valve connected at the mouth of the rotary pump.

The temperature profile of the furnace measured from the centre position of the furnace is shown in Figure 2-4. The temperature gradient shows a Boltzmann type profile. Here the source material is placed in a quartz boat and this boat is placed inside the chamber where temperature is maximum. The substrates are placed in downstream direction at the elevated temperature regions which is a few cm apart from the centre positions. The temperature ramping rate of the furnace was maintained at a fixed value of 15°C/min. When the temperature of the furnace is reached the maximum set value, the ZnO powder vaporizes and it is carried by the carrier gas (Ar) to the substrate positions. The flow of the carrier gas is controlled precisely by using a mass flow controller (Sevenstar, China). During the process, the Zn/ZnO vapor is sufficiently reacted with the substrate and condensed, which results in the growth of ZnO NWs/NRs.
Figure 2-3. (a and b) Photograph and schematic diagram of the in–housed developed thermal vapor deposition setup, respectively.

Figure 2-4. Temperature profile of the HT furnace used in the TVD setup. Temperature is monitored inside the chamber using a K–type thermocouple.
The detailed description of the growth of ZnO NWs/NRs over a range of temperature is explained below in stepwise. We study the effects of several growth parameters on the morphology of the as–grown products. The growth of NWs/NRs by vapor deposition process includes substrate cleaning, substrate preparation and vapor deposition processes.

A. Substrate Cleaning: The substrate used for the growth of the NWs/NRs is commercially available nominally $n$–type doped Si (100) wafer (University wafers, USA). Si wafer is first cleaned in acetone and then trichloroethylene under ultrasonic bath for 15 mins each to remove impurities and organic grease. The native oxide layer is etched out with 10% hydrofluoric acid solution for 60 sec. After each step, substrate is rinsed with de-ionized water several times and finally dried with N$_2$ gas blow.

B. Substrate Preparation: For self-catalytic growth of NWs/NRs, we have used very thin layer of ZnO. ZnO seed layer is deposited on the pre–cleaned Si(100) substrates by using the RF magnetron sputtering system. Sputtering is carried out at incident RF power of 100 W for different time duration at substrate temperature of 300°C at high vacuum of $4 \times 10^{-6}$ mbar. A mixture of argon and very low concentrated oxygen are used as reacting gases during sputtering. During deposition, the chamber pressure is maintained at a fixed value of 0.008 mbar. For self–catalytic growth of ZnO NWs about 200 nm thick ZnO seed layer is used. The thickness of the deposited layer is estimated from the deposition rate and further confirmed from surface height profile measurement (Dektak 150, Veeco, USA).

C. Vapor Deposition: We use ZnO nano powder (Sigma–Aldrich, USA, purity 99.999%, average size 50–70 nm) and Zn$_{1-x}$Co$_x$O powder as source material for the growth of ZnO NWs and NRs by vapor deposition method to study the structure, morphology and doping effect of the final products. As the melting point of ZnO is very high (1975°C), we used high quality graphite powder (Fluka, USA, purity 99.99%,) as the reducing agent. Therefore, mixture of ZnO and graphite powder is loaded at the centre positions of the furnace inside the TVD chamber. During heating, a carbothermal reaction takes place which produces zinc and zinc suboxide vapor in the temperature range 900–1000°C. This vapor is transported by carrier gas, Ar to the elevated temperature regions. Then the
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The vapor mixture is deposited on the substrate. The chamber pressure is maintained at 1.3 mbar during the growth. In this case, at HT the ZnO seed layer absorbs the incoming vapor and after condensation growth of NWs/NRs has been started. Prolonged condensation might result in the growth of vertically aligned ZnO NWs/NRs.

2.4 Characterization Techniques

Several scientific tools have been utilized to characterize the different DMSs samples. As analytical characterization, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM) and x–ray diffraction (XRD) techniques are used to know the morphology, orientation, structure and crystal phase of the ZnO NSTs. Micro–Raman spectroscopy, UV–Vis spectroscopy, photoluminescence (PL) spectroscopy are used for spectroscopic study. XPS measurement is carried out with a fully automated XPS microprobe (PHI X-tool, ULVAC-PHI) using Al Kα x-ray beam (1486.7 eV) with beam current of 5 mA. The magnetic properties of the samples are examined by using a Lakeshore vibrating sample magnetometer (VSM) (Model no. 7410) and Superconducting Quantum Interface Device (SQID).

2.4.1 Analytical Techniques

In this section we will present the brief description of the tools used for the analytical characterization of the different DMS NSTs. Sample preparation for imaging as well as for specific measurements are also discussed in detail.

2.2.1.1 Field–Emission Scanning Electron Microscopy (FESEM)

The FESEM is a very useful tool for high resolution surface imaging in the fields of nanomaterials science. The FESEM use a field of electrons to probe objects on a very fine scale. The use of electrons has two main advantages over optical microscopes: much larger magnifications are possible since electron wavelengths are much smaller than photon wavelengths and the depth of field is much higher. The electron wavelength \( \lambda_e \) depends on the electron velocity \( v \) or the accelerating voltage \( V \) as
The photograph of the FESEM (Sigma, Zeiss, Germany) used in the present study is shown in Figure 2-6. In the FESEM, field emission gun is used which utilizes field-emission effect. Field emission is the emission of electrons from the surface of a conductor caused by a strong electric field. An extremely thin and sharp tungsten needle (tip diameter 10–100 nm) works as a cathode. The FE source reasonably combines with conventional scanning electron microscope (SEM). The acceleration voltage between cathode and anode is commonly in the order of magnitude of 0.5 to 30 kV, and the apparatus requires an extreme vacuum (~10^{-9} \text{torr}) in the column of the microscope. After the emission, the electrons are then accelerated off of the source by two anodes.

\[ \lambda_e = \frac{h}{mv} = \frac{h}{\sqrt{2qmv}} = \frac{1.22}{\sqrt{V}} \text{ nm} \]

\[ \text{..............................(2.1)} \]

Because of the microscopic size of the electron source, the beam produced by this emitter is about 1000 times smaller than that in a standard SEM, which markedly improves the image. That beam is collimated by electromagnetic condenser lenses, focused by an objective lens, and scanned across the surface of the sample by electromagnetic deflection coils. The primary imaging method is by collecting emitted secondary electrons.
electrons that are released by the sample. A secondary electron detector is placed near to the specimen. By correlating the sample scan position with the resulting signal, an image is formed on the screen that is strikingly similar to what would be seen through an optical microscope. The FESEM is equipped with a special objective or focusing lens that projects the magnetic field below the lens. Very high resolution is obtained by shortening the specimen–lens distance and using a specially designed in–lens. The distance is shortened by placing the specimen in the lens magnetic field. In this case, secondary electron detector is placed above the objective in–lens (called as in–lens detector), which makes different in the image compared to the conventional image of the secondary electron detector. Very high resolution and contrast can be obtained by using in–lens detector.

For the sample preparation of the FESEM imaging, Si substrate containing NWs was directly mounted on the FESEM stub using a carbon coated tape. Here the carbon tape is used as adhesive and also provides an electrical conduction to the sample.

2.2.1.2 Transmission Electron Microscopy (TEM)

TEM is one of the best characterization techniques of nanophase materials with resolution close to atomic level. By combining TEM with selected area electron diffraction (SAED) pattern, a wealth of information, such as NWs growth direction, defect or dislocation, crystallinity, and lattice constants can be studied. A schematic diagram of a TEM is shown in Figure 2-7. It works on the principle of optical projection; when an object is placed in front of a light source, its image is enlarged and shadow is created on the screen placed far distance behind this object. Electrons emitted from an electron gun are accelerated to high voltages (typically 100 to 400 kV) and focused on the sample by the numbers of condenser lenses. We used a lanthanum hexaboride (LaB6) crystal for thermionic electrons emission. The emitted electrons pass through a series of lenses to be focused and scanned across the sample. The sample is placed on a small copper grid a few mm (~ 3mm) in diameter. The static beam has a diameter of a few microns. The sample must be sufficiently thin (a few tens to a few hundred nm) to be transparent to electrons. The transmitted and forward scattered electrons form a
diffraction pattern in the back focal plane and a magnified image in the image plane. With additional lenses, either the image or the diffraction pattern is projected onto a fluorescent screen for viewing or photographic recording. High resolution TEM (HRTEM) gives structural information on the atomic size level, is known as lattice imaging, and has become very important to know the NWs growth direction, lattice parameters and presence of any defects/dislocations.

In the present study, a 200kV TEM (JEM2100, JEOL, Japan) with high resolution CCD camera (Gatan, USA) is used for the normal TEM and HRTEM imaging. Sample for the TEM imaging was prepared by transferring the NWs into a methanol solution. A transparent dispersion of NWs was made by sonication and then drop casted on the

Figure 2-6. Schematic diagram of the transmission electron microscopy used for the structural characterization of the NSTs.
carbon coated copper grid containing few hundreds of square shaped hollow meshes with
dimension of 1µm. After normal dry for prolong time this grid is used for TEM imaging.
Improved resolution of the lattice image is obtained after processing of fast Fourier
transformation (FFT) using 'Digital Micrograph' (Gatan, USA)' image analysis software.
In addition, we used SAED to get information about crystallinity and growth direction of
the ZnO NWs.

2.2.2.1 X–ray Diffraction (XRD)

XRD is the most widely used non–destructive technique for general crystalline material
characterization. The XRD patterns provide information on crystal phase, lattice
parameter, strain and preferred growth direction of the NWs. In XRD a collimated beam
of x–rays, with wavelength λ=0.5–2.0Å, is incident on a specimen and is diffracted by the
crystalline phases in the specimen according to 'Bragg's law',

\[ 2d\sin\theta = n\lambda \] .................................(2.2)

where \( d \) is the spacing between atomic planes in the crystalline phase, \( \theta \) is the angle of
incidence of the x–ray beam with the atomic plane, \( n \) represents the order of diffraction
(we consider only the first order diffraction, \( n =1 \)). The intensity of the diffracted x–rays
is measured as a function of the diffraction angle 2\( \theta \) and the specimen's orientation. In the
present study, the Seemann–Bohlin geometry is used,\textsuperscript{264} where the incident x–rays
impinge on a fixed specimen at a small angle 1–5° and the diffracted x–rays are recorded
by a detector that moves along the focusing circle. This method provides good sensitivity
for thin films, due to parafocusing and the large diffracting volume. Owing to the huge
data bank available from JCPDS Powder Diffraction Files covering practically every
phase of every known material, crystal phase of the sample is identified from the peak
positions of the diffractogram. Homogeneous or uniform elastic strain in the (hkl)
direction can also be calculated from the shift in the diffraction peak positions, and the
\( d_{hkl} \) spacing of the unstrained crystal.

X–ray diffraction patters of the NSTs were obtained using a commercial XRD (Seifert
3003 T/T, GE, USA) using a CuK\( \alpha_1 \) (\( \lambda=1.5406 \) Å) radiation or Mo X–ray radiation
(\( \lambda=0.7093\)Å) with nickel filter. A photograph of the XRD machine is shown in Figure
2-8. All the data are taken at room temperature in thin film mode at a grazing angle of 3°. All

Figure 2-7. Photograph of the x–ray diffractometer (Seifert 3003 T/T, GE, USA) used for the structural characterization of the NWs.

measurements were carried out at an accelerated voltage of 40 kV and tube current of 30 mA. The scanning step size and sampling time were 0.05 and two second, respectively. The exact peak position and FWHM of the XRD peak is obtained from the Lorentzian fitting to the experimental peak position, using following expression

\[
y = y_0 + \frac{2A}{\pi} \frac{w}{4(x-x_c)^2+x^2}
\]

.................................(2.3)

Where \(y_0\) is the offset constant, \(x_c\), \(w\) and \(A\) are the peak position, FWHM and area, respectively. FWHM gives the crystallite size and lattice strain is calculated from the shift in \(x_c\) from the \(x_c\) in unstrained sample.

2.4.2 Spectroscopic Techniques

In this section we present a brief description of the tools used for the spectroscopic characterization of the DMS NSTs. The spectroscopic data analysis techniques used in the present study are also discussed.
2.2.2.1 Micro–Raman Spectroscopy

Micro–Raman spectroscopy is a vibrational spectroscopic technique use to characterize many properties (such as crystallinity, strain, and oxygen vacancy) of ZnO bulk and NSTs. It is based on the Raman scattering process that corresponds to the interaction between incident photons and the optical phonons. During Raman spectroscopy measurement, an intense laser beam is incident on the sample through a commercial microscope with spot size about few microns. The weak back–scattered light or signal from the sample is passed through a double monochromator to reject the Raleigh scattered light and the Raman–shifted wavelengths are detected by a photodetector or CCD detector. The lines become very broad for amorphous semiconductors, allowing a distinction to be made between single crystal, polycrystalline, and amorphous materials. Raman spectral profile contains information about structure, crystallinity, strain and phonon confinement effects in NWs. The frequency of the Raman signal is also shifted by stress and strain in NWs. Both compressive and tensile stress can be determined with compressive stress giving an upward and tensile stress a downward shift compared to the peak position of the unstrained crystal.

We used a high resolution micro–Raman ((LabRAM HR–800, Jobin Yvon, USA) with liquid nitrogen cooled CCD detector. The photograph of the micro–Raman setup used in the present study is shown in Figure 2-9. All the measurements are carried out at room temperature using a 488 nm Ar⁺ laser at a resolution of 0.3 cm⁻¹. The laser power at the sample side was fixed at approximately 0.9 mW.
Figure 2-8. Photograph of the micro–Raman spectrometer (LabRAM HR–800, Jobin Yvon, USA).

Figure 2-9. First–principles calculated phonon dispersion curve of hexagonal wurtzite (WZ) structured ZnO crystal. Adapted from Ref. [206].
ZnO in hexagonal wurtzite structure belongs to the space group $P6_3\overline{mc}$ which has two formula units in the primitive cell. For a single crystalline ZnO, at $\Gamma$ point of the Brillouin zone, it has eight sets of optical phonon modes,\textsuperscript{206} which is shown in phonon dispersion curve of pure hexagonal ZnO in Figure 2-10. They are $A_1 + E_1 + 2E_2$ modes which are Raman active, $2B_1$ modes which are Raman silent and $A_1 + E_1$ modes which are infrared active. The polar modes of $A_1$ and $E_1$ are splitted into tranverse (TO) and longitudinal optical (LO) phonon, while the nonpolar modes of $E_2$ have two frequencies identified as $E_2^{\text{high}}$ and $E_2^{\text{low}}$ associated with oxygen atoms and Zn sublattice, respectively.\textsuperscript{207} $E_1^{\text{LO}}$ mode is caused by the defects such as oxygen vacancy, zinc interstitial or their complex, which enables to identify the defects present in the ZnO NSTs. Compared to bulk ZnO, the decreased dimensions of ZnO NWs lead to spatially confined phonons, giving rise to the phonon quantum confinement effect. Characteristics of phonon confinement could be:\textsuperscript{208} (1) frequency downshift and Raman line shape broadening, whereas structure defects and residual stress could also contribute to the phonon linewidth broadening; and (2) generation of new features absent in the corresponding bulk spectrum. Raman spectrum typically shows Lorentzian line shape. Experimental data is analyzed by fitting multiple peaks with Lorentzian peak shape profile to extract the peak parameters.

2.2.2.2 X-Ray Photoelectron Spectroscopy

The chemical composition and the ionic states of as synthesized DMS materials were investigated using a scanning ESCA (Electron Spectroscopy for Chemical Analysis) microprobe (PHI Quantum 2000). When a material is exposed to electromagnetic radiation of sufficiently high energy, the emission of electrons is observed. This phenomenon is known as the photoelectric effect. A high energy photon, which $h\nu$ is significantly in excess of the threshold energy $h\nu_0$ may be capable of separating one photon/one electron photoionization event by ionizing different species of electrons having various ionization energies $I_k < h\nu$. One photon may eject a very loosely bound electron, imparting high kinetic energy to it, while another photon of the same energy
might ionize a more tightly bound species of electron and produce a photoelectron of lower kinetic energy. Since the energy levels occupied by electrons are quantized, the photoelectrons have a kinetic energy distribution \( n(E) \), consisting of a series of discrete bands that essentially reflect the 'shell' form of the electronic structure of the sample. The experimental determination of \( n(E) \) by a kinetic energy analysis of the photoelectrons constitutes photoelectron spectroscopy. Ejection of photoelectrons is a very direct way of obtaining information and characteristics of atoms. If high enough excitation energy is provided, core level spectra can be obtained for all elements in the periodic table except H and He, and the determined binding energies of these core levels are sufficiently unique for their unambiguous identification. XPS will give valuable information about the surface functionalities, compositions and chemical states of the material.

Figure 2-2-10 XPS microprobe (PHI X-tool, ULVAC-PHI) with Al K\( \alpha \) x-ray beam (1486.7 eV)
2.2.2.3 Photoluminescence (PL) Spectroscopy

In PL spectroscopy, one measures physical properties of the material by shining photons to excite electrons to higher energy levels and analyzing the optical emission as these states relax. The spectral distributions of the emission are related to electronic transition probabilities within the sample. Photoexcitation causes electrons–holes generation within the material and that electrons move into permissible excited states. When these electrons return to their equilibrium states, the excess energy is released and electron and a hole can either recombine non–radiatively by emitting phonons (or transferring energy to other particles) or radiatively by emitting photons. The energy of the emitted light (PL) relates to the difference in energy levels between the two electronic states involved in the transition between the excited state and the equilibrium state. The PL spectroscopy measures the count of emitted photons in a spectral range. The PL spectroscopy provides quantitative information like exciton transition, exciton binding energy, trap states, impurities states etc. From PL spectrum information of the radiative defects present on the samples could be obtained. An excellent review of photoluminescence spectroscopy of crystalline semiconductors has been given by G.D. Gilliland.209

We used a high sensitive steady–state fluorimeter (FS920P, Edinburgh Inst. UK) in the present study. The photograph of this instrument is shown in Figure 2-11. A He–Cd continuous laser (Kimmon Koha, Japan) of wavelength 325 nm is used to excite the samples. The emitted photons are captured using standard single photon counting detector tube. It has two grating monochromator, one at the excitation side and other one at the emission side. The monochromators have computer controlled slits and the spectrometer software displays the band with settings in nm units, taking automatically into account the opto–mechanical properties of the grating. The steady state PL peaks are usually Gaussian in lineshape expressed by

\[ y = y_0 + A \exp \left[ -\frac{(x-x_0)^2}{2w^2} \right] \]

..............................(2.16)
Where $y_0$ is the offset constant, $x_c$, $w$ and $A$ are the peak position, width and peak amplitude, respectively. $w$ multiplied by $\sqrt{2\ln 2}$ gives the exact value of FWHM of the Gaussian profile. The measured spectral profile of the PL spectrum is analysed by fitting with Gaussian lineshape function or combination of number of this function using PeakFit software.

**Figure 2-11.** Photograph of the steady–state photoluminescence spectrometer (FS920P, Edinburgh Inst., UK).

### 2.2.2.4 UV–Vis Spectroscopy

This technique is used to study either reflection or absorption or transmission properties because the electronic band structure of semiconductors and metals are determined by their optical properties. The optical reflection or absorption is a result of interaction between the material and light. In the present case we have grown the ZnO NWs on the Si substrate. As the Si is an opaque substrate in the UV–Vis region, there is a limitation in optics for the direct measurement of the absorption of the ZnO NWs. Therefore, we measured the specular reflectance at an angle of $45^\circ$. In the measurement of specular reflectance, the detector collects only those reflected signals having angle of reflectance is equal to the angle of incidence. Then we used this data to calculate the absorption coefficient of the ZnO NWs in the UV–Vis region. The absorption coefficient, $\alpha$ is calculated for each wavelength in this region according the method proposed by Rusli et al.\textsuperscript{210}
2.4.3 Vibrating Sample Magnetometer (VSM) and SQUID

The various field dependent and temperature dependent magnetic properties of the DMS nanostructures and thin films are measured by VSM and SQUID. Fully integrated vibrating sample magnetometers (VSM) are used for the characterization of materials’ DC magnetic properties with respect to time, temperature and magnetic field in Lake Shore's setup.

The VSMs have three different modes: 1) single-stage variable temperature option 2) magnetoresistance (MR) probe option; 3) high temperature oven/ low temperature cryostat.

All the three modes have different variable gap electromagnet configurations with magnetic fields up to 2T. The VSMs are sensitive electromagnetic systems with a wide range of capabilities from 4.2K to 1273K. They can measure a wide range of samples, making them suitable for quality control of magnetic materials and all demanding materials research applications. SQUID can be used to measure extremely weak magnetic signals.

Figure 2-12 (a) Lake Shore VSM setup, (b) SQUID setup