2
Fabrication and Characterization Techniques

2.1 INTRODUCTION

To achieve high quality ZnO nanorods and nano-crystalline thin film deposition, physical vapor deposition techniques like RF sputtering technique is an inevitable compulsion since few years. Due to demand inflation of 1-D nanostructure based sensors in the field of optoelectronic devices and gas sensors, deposition of well aligned nanorods and nano-crystalline thin films is highly essential. And the quality of metal contacts also plays an imperative role in electrical or gas sensing characterization of nano-devices. Thus, in first section, working principles of RF sputtering and thermal evaporation techniques have been explained for deposition of high quality ZnO nanostructures and metal contacts. Irradiation techniques have been used for modifying material properties. Then, various structural, surface morphology, optical and electrical characterization techniques such as XRD, AFM, FESEM, CL and PL spectroscopy, Raman Spectroscopy and I-V have been explained. Lastly, characterization of gas sensing for ZnO nanostructure based hydrogen sensor have also been reviewed.

2.2 DEPOSITION TECHNIQUES

2.2.1 RF Sputtering

RF sputtering is one of the most popular physical vapor deposition (PVD) technique for insulator material deposition and is widely used in mass production of metals and semiconductors. It has few advantages like deposition in low temperature, good adhesion of thin films or nanostructures with substrate, possibility of substrate variation, low cost etc. which makes it an efficient deposition technique. When a material is bombarded by high energy ions, material's surface gets sufficient energy to extract atoms from target material and these atoms travel towards substrates and the whole process is called sputtering. In RF sputtering, sputtering target and substrate are placed in high vacuum chamber. RF sputtering target is then mounted on RF magnetron which act as cathode and substrate is placed on substrate holder which behaves as an anode. The substrate holder is mounted on substrate heater which heats substrate uniformly to achieve desirable deposition temperature. For creating high vacuum (~10^{-6} mbar) in deposition chamber, rotary pump followed by turbo pump is used. By creating high vacuum, possibility of contamination on deposited nanostructures is reduced. For sputtering, inert argon gas and reactive gases like oxygen and nitrogen are filled into sputtering chamber at constant flow rates controlled by mass flow controller (MFC). The basic sputtering parameters such as RF power, target to substrate distance, gases flow rates, chamber pressure and substrate temperature have major impact on quality of deposited nano-crystalline thin films and nanorods. By varying these sputtering parameters and controlling various structural, optical properties and surface morphology, large deposition area can be attained. Figure 2.1 depicts pictorial representation of RF sputtering technique.

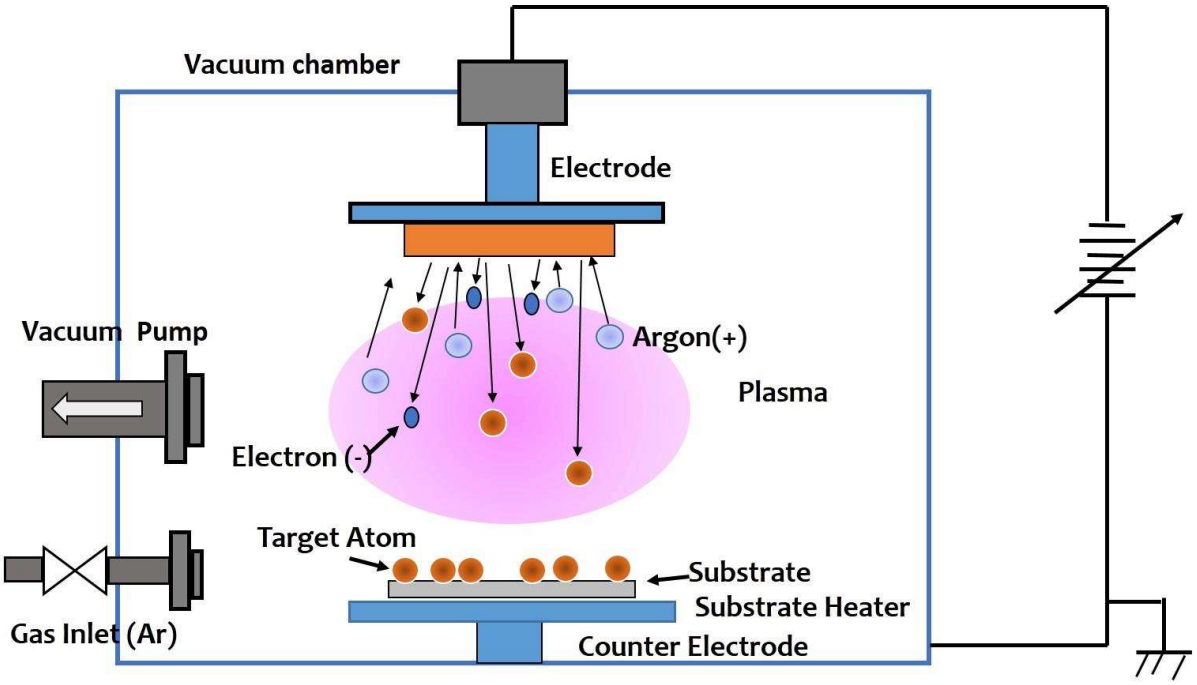

Figure 2.1: Pictorial representation of RF sputtering technique

In sputtering process, high vacuum of about 10^{-6} mbar has been created to create mean free path for sputtering gas flow with minimum environmental contamination. Initially, inert gas (Ar) of 99.999% high purity is flown into sputtering chamber at constant flow rates to maintain constant pressure in sputtering chamber. Typically, argon is used as sputtering gas due to its high atomic weight and non-reactive nature. By increasing argon flow rates, dense plasma can be created in chamber for increasing sputtering rates. When constant RF power is applied between target magnetron and substrate plate, RF voltage changes its polarity between cathode and anodes which establishes an electric field between them. In initial phase, when substrate plate has positive voltage in comparison to target, high energy electrons withdraws from the target and accelerates towards substrate and collides with inert argon atoms present in the path. Due to such collisions, positive argon ions (Ar^+) and secondary electrons are generated and further collision by these secondary electrons produces large number of argon ions and forms a dense plasma in sputtering chamber. And as RF power becomes negative at target magnetron, more high energy positive argon ions get attracted towards sputtering target and collides with target material and extracts target atoms. These atoms then travel through chamber towards the substrate. Consequently, process of deposition of target material on the substrate takes place. And sputtering yield can be changed by varying deposition parameters. Reactive gases such as oxygen and nitrogen are also used in sputtering with an aim to achieve oxide and nitrite films/nanostructures. Figure 2.2 shows experimental setup of RF sputtering (Hind high vacuum combined RF/DC sputtering system).

Figure 2.2: Experimental setup of RF sputtering (Hind High Vacuum combined RF/DC Sputtering System)

2.2.2 Thermal Evaporation

This technique is most widely used thin film deposition techniques amongst other physical vapour deposition (PVD) methods. In thermal evaporation, vacuum deposition method is used for deposition of various metals and non-metals over various substrates including oxides and nitride pure materials. The deposited thin films thickness can be varied from few nm to micrometer range by varying deposition time and evaporation rate related to filament's current. Single layer and multi-layer thin film deposition is also possible through this method. To avoid environmental contamination throughout the process, high vacuum of 10^{-6} mbar is built at the initial stage with the help of rotary and turbo pump. Then, source material is heated up to its melting point where vapour clouds are formed inside the vacuum chamber. Due to low pressure in vacuum chamber, these vapour clouds travel in upward direction towards the substrate and sticks to the substrate after collision in the form of thin film. Since, substrate has lower temperature, vapour molecules transfer energy to substrate, gets condensed on to the surface and forms a thin deposition layer. High temperature can be sustained by heating source material either by resistive heating filaments or by thin sheet metal boats. These heating filaments or boats are made up of tungsten, molybdenum or tantalum and selection of heating elements depend on either heating temperature or reaction with source materials. In this technique, generally, source material is placed on heating filament or boat located at the bottom of evaporation chamber and substrate is mounted upside down at the top of chamber. When low voltage and high current is applied to these heating filaments, source material melts down due to high temperature induction and get vaporized towards the substrate. Such evaporation technique gives a uniform step coverage and adhesion onto the substrates. An approximated thickness of deposited thin film is calculated with the help of thickness monitor mounted at the top of substrate holder [Semicore Equipment, Inc., 2016]. Figure 2.3 and 2.4 depicts pictorial representation and experimental setup (Semicore Thermal/e-Beam evaporation system) of thermal evaporation system, respectively.

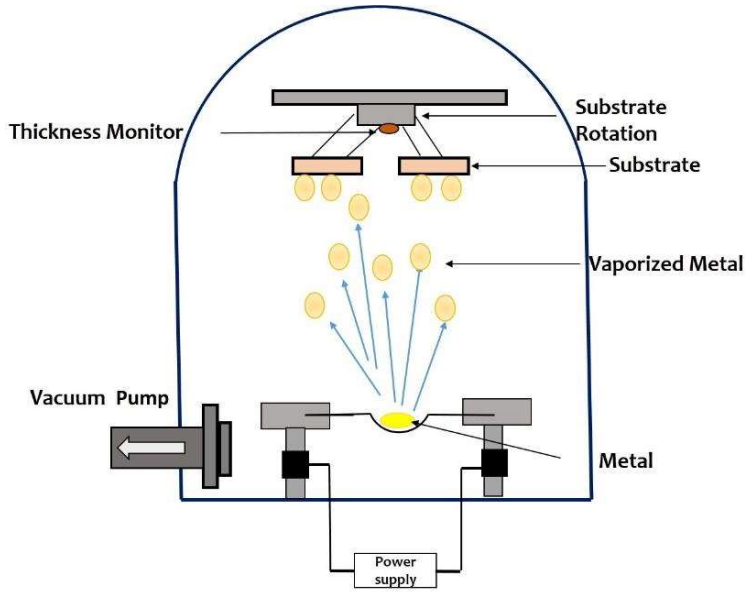

Figure 2.3: Pictorial representation of thermal evaporation system

Figure 2.4: Experimental setup of thermal evaporation system (Semi-core Thermal/e-Beam evaporation System)

2.3 IRRADIATION TECHNIQUES

When source material is exposed to the radiation, it is called irradiation process. Irradiation processes may have generated by various radiation source which either are in the form of ion irradiation or non-ionized radiation. By varying irradiation fluences and irradiation source, material properties such as optical, electrical, crystallinity and surface morphology can be modified.

2.3.1 Gamma Irradiation

For gamma irradiation, Co-60 gamma rods were used as uniform irradiation source and were placed at the boundary walls of gamma exposer chamber. This exposer chamber was highly packed due to which, radiation leakage was minimal. The nanosensor device was vertically mounted in the centre of irradiation chamber and was uniformly exposed from all sides. Gamma irradiation chamber was irradiated at dose rate of 3 kGy/hr at room temperature when constant power was applied to the chamber. By varying irradiation time, irradiation doses of desired level can be obtained. Figure 2.5 depicts schematic diagram of gamma irradiation chamber at Defence lab, Jodhpur [Source: Barala *et al*., 2015].

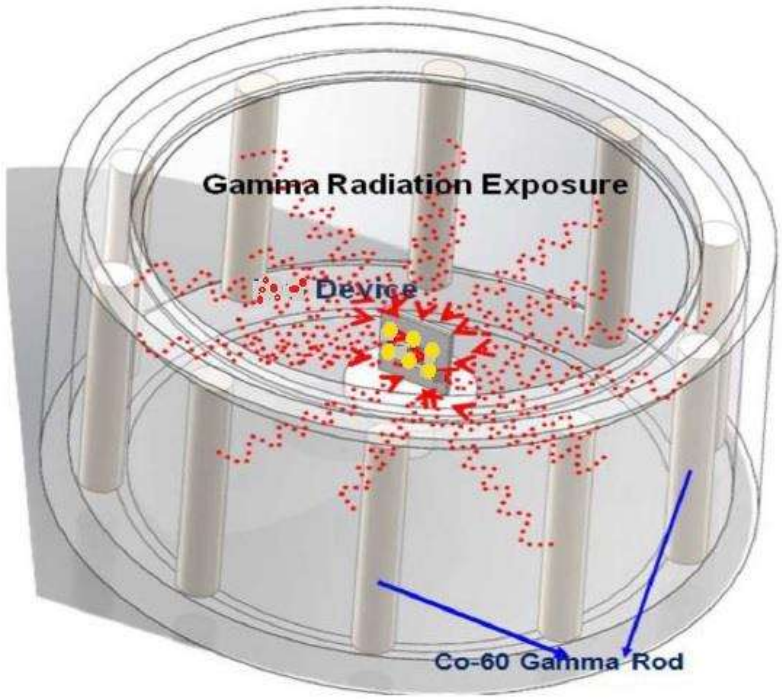

Figure 2.5: Schematic diagram of gamma exposer chamber for gamma Irradiation (Source: Barala *et al*., 2015)

2.3.2 Swift Heavy Ion Irradiation (SHI) Technique

Swift heavy ion irradiation technique is a powerful tool to modify material properties. Swift heavy ion irradiation facility is available at Inter University Acceleration Centre (IUAC), New Delhi. The centre has 15 UD pelletron accelerator [IUAC, New Delhi] that can accelerate various ion species with energy varying from few MeV to hundreds of MeV. Figure 2.6 shows schematic diagram of chamber of 15 UD pelletron accelerator at IUAC, new Delhi. These accelerator have a stainless steel tank that has high voltage terminal in middle section of the chamber, where irradiation takes place in beam line in a high vacuum chamber. When ions get sufficient high energy, they are accelerated towards the terminal.

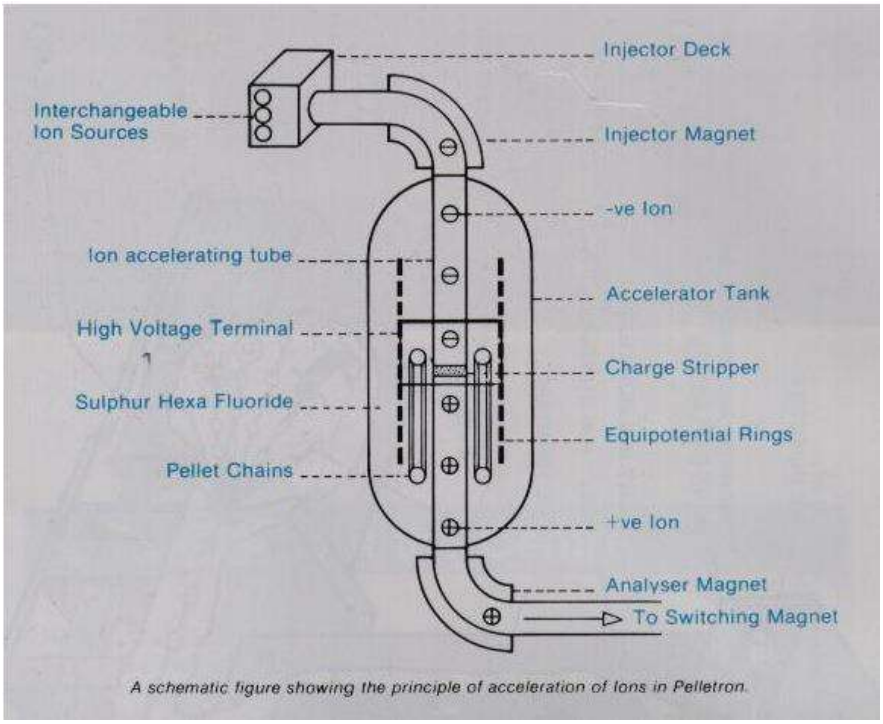

Figure 2.6: Schematic diagram of chamber of a 15 UD pelletron accelerator at IUAC, New Delhi (Source: IUAC, New Delhi)

2.4 CHARACTERIZATION TECHNIQUES

2.4.1 X-Ray Diffraction (XRD)

X-Ray diffraction is a powerful technique used for structural characterization. X-Ray diffraction is widely used to study crystal structure, grain size and their orientation, in-plane stress/strain calculation and their chemical composition for crystalline thin films or structures [Cullity, 1978]. In each crystal structure, atoms are arranged in specific orientation which forms a crystalline microstructure. Basic working principle of X-ray diffraction is based on constructive interference of monochromatic X-rays and crystalline planes of samples. These X-rays are generated by cathode ray tubes having Cu-Kα as radiation source with 1.54 A° X-ray wavelength. X-rays penetrates through filters to achieve monochromatic radiation. Then they pass through collimator and are finally directed towards thin film samples or powder samples. The diffracted rays have been collected by detector. These X-rays scanned for all 2θ diffraction angle which gives possibility of all diffraction direction in crystal structure. Each crystal has a unique fingerprint for specific plane and so, we can extract crystalline plane information using 2θ-ω scan. Incident X-ray's incident on sample at angle θ and get diffracted from crystalline planes which satisfied Bragg's diffraction law [Guinebretiere, 2006].

Bragg's diffraction law is given by:

$$n\lambda = 2d\sin\theta \quad (2.1)$$

where d is interplane space in crystalline structure, θ is angle of incident, λ is X-ray wavelength (1.54 A°) and n=1 for constructive interference. Figure 2.7 shows schematic diagram of Bragg's X-ray diffraction and Figure 2.8 gives X-ray diffraction system (D8 Advance,Bruker).

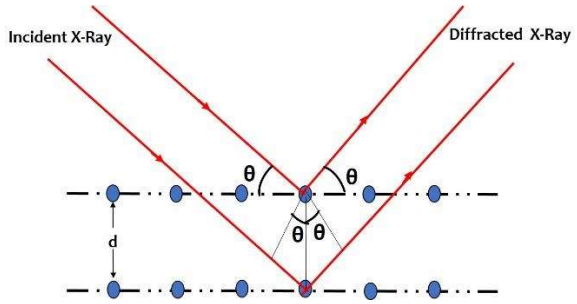

Figure 2.7: Schematic diagram of Bragg's x-ray diffraction

Figure 2.8: X-Ray diffraction system (D8 Advance, Bruker)

2.4.2 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is one of the most powerful technique for measuring surface morphology of various kinds of samples with minimum sample preparation and gives three dimensional topography with high resolutions. In AFM, scanning sharp tip with diameter in range of few nm mounted on free end of cantilever which made by either silicon or silicon nitride. The cantilever mounted on tip holder which always attached with scanner. When cantilever tip comes in to contact with sample, due to presence of forces between tip and sample surface, cantilever got deflected. AFM measured these forces in terms of either mechanical forces or van der walls forces etc. According to detection of these forces, AFM defines mode of detection either contact mode or non-contact mode. In non-contact mode, cantilever tip vibrates over sample with 100-400 kHz frequency with very small amplitude. The distance between cantilever tip and sample surface is in order of few angstroms. When these tip comes closer to sample surface in range of van der wall forces, repulsive force acted on these resonating cantilevers.

However, if distance between tip and sample surface increases, attractive force brings back tip in van der wall forces range. Thus cantilever got deflected either towards sample surface or away from sample surface which depends on surface morphology (height variation of sample). A laser beam is focused on cantilever free end which almost above on cantilever tip position. These lasers got reflected by top side of cantilever, there is slight variation in reflected laser rays as cantilever deflects according to surface morphology. These reflected ray has been captured by photo detector which measure these cantilever deflections in z direction at each x-y position. By using feedback controller, constant position of these AFM tip could be maintained over surface. Thus measuring distance between tip to sample at each x-y point, electrical signal generated and scanning software construct sample morphology even for nm scanning range. Figure 2.9 shows schematic diagram of AFM imaging and Figure 2.10 shows instrument setup for AFM at IIT Jodhpur (Park XE-70).

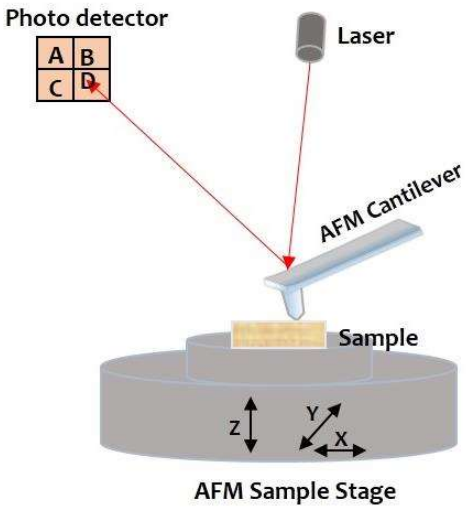

Figure 2.9: Schematic diagram of AFM imaging

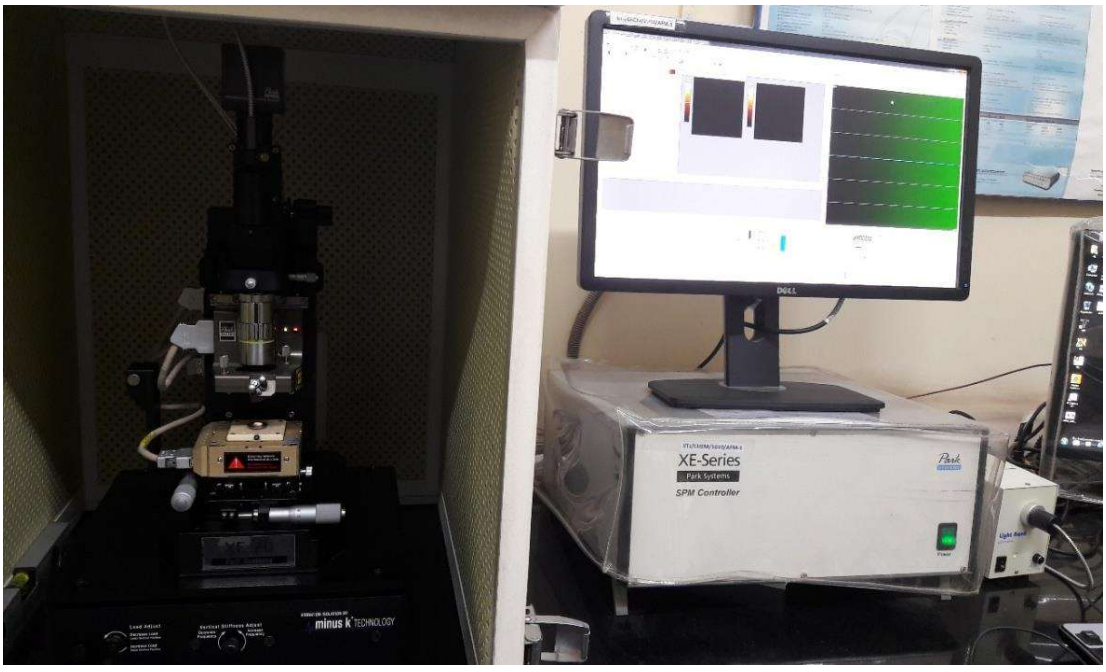

Figure 2.10: Instrument setup for AFM at IIT Jodhpur (Park XE-70)

2.4.3 Field Emission Scanning Electron Microscopy (FESEM)

FESEM is a very useful tool for studying surface morphology, size and shape distribution, thickness monitoring and high resolution surface imaging possible. The surface topography with material composition and electric conductivity can be achieved using these characterizations. In this characterization, high energy electron beam of narrow pointed shape tip is scanned over desired surface of sample, giving high resolution images of target surfaces. Initially electron gun emits high energy electron beam followed by field emission cathode which narrowing electron beam at low and high energy. In lens, Schottky field emission source used as electron source. The accelerating voltage between anode and cathode have been used in order of 0.2 kV to 30 kV. To focus these primary electrons, high vacuum (~10^{-6} Pa) required in column of microscope. To produce narrowing focused electron beam, electromagnetic lenses used for focusing and defected these beam. To achieve high resolution surface morphology with sharp features, beam diameter should be smaller than features size. These FESEM have high resolution image quality as for 3 nm at 1kV and 1.2 nm at 30 kV. These also gives high magnification range varies from 10x to 10^6 x for achieving few nm surface morphology. When these high energies focused electron beam bombarded each spot on surface, secondary electrons emitted from each spot. These secondary electrons have been captured by detector and it's generate signal which creates topography. The velocity and angle of emission of each seconder electron gives information about surface structure at each spot. We used JEOL JSM- 7100F FESEM system at university of Nova Gorica (material research laboratory), Slovenia. Figure 2.11 shows sematic diagram of FESEM characterization and Figure 2.12 shows JEOL JSM-7100F FESEM instrument.

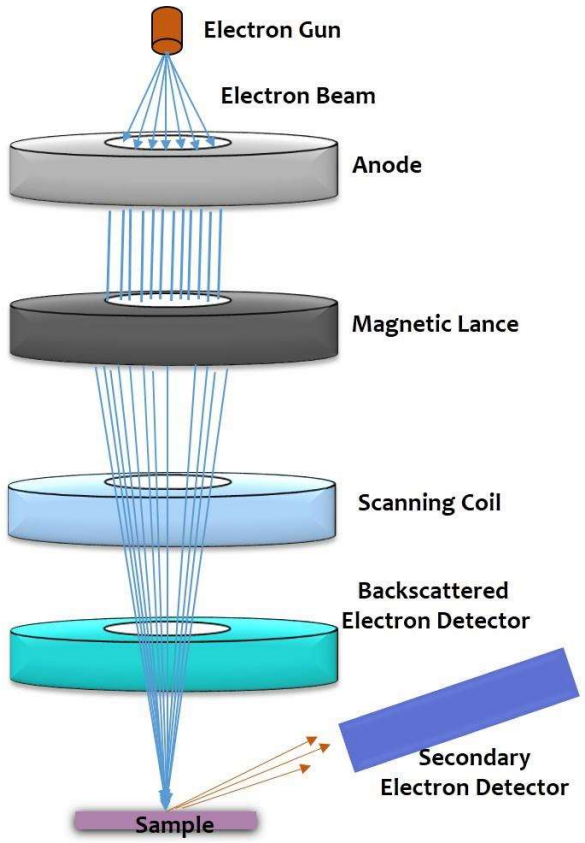

Figure 2.11: Schematic diagram of FESEM characterization

Figure 2.12: JEOL JSM-7100F FESEM instrument (Source: University of Nova Gorica, Slovenia / Material Research Lab.)

2.4.4 Cathodoluminescence Spectroscopy (CL Spectroscopy)

In CL spectroscopy, optical characterization including optical band gap with crystal defects and electrical properties presents in semiconductor, can be analysed using CL spectra. Initially high energy electron beam focused to semiconductor material which leads to large number of secondary electron emission by inelastic scattering mechanism in to crystal. These primary high energy electrons transfer energy to crystal which excite secondary electron from valance band to conduction band. When these excited electrons go back to valance band, its emit photons. These emitted photons could be reflected by elliptical mirrors and passes through optical fiber and its compound wavelength spectra at each x-y point recorded. We used MONO CL4 Gatan cathodoluminescence spectroscopy (SEM-CL) at University of Nova Gorica, Slovenia. It recorded near band and visible region spectra which coupled with FESEM and operated with 7nm band width (~0.06 eV at 3.24 eV). Figure 2.13 depicts schematic diagram of CL spectroscopy [Furukawa *et al.,* 2013].

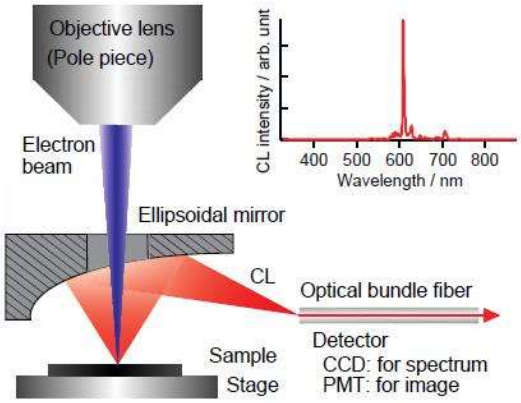

Figure 2.13: Schematic diagram of CL spectroscopy (Source: Furukawa *et al.*, 2013)

2.4.5 Photoluminescence Spectroscopy (PL Spectroscopy)

Photoluminescence spectroscopy is an optical characterization technique to find out basic properties of materials such as optical band gap, impurities etc. When monochromatic light with particular wavelength falls on material, electron gets excited so as to reach excitation state. This whole process is known as photon excitation. When these excited electrons returns to conduction band by emitting photon, the process is called photoluminescence. In PL spectroscopy, light source emits wide range of wavelengths which further passes through excitation monochromatic. These monochromator passes only specific wavelengths that falls upon the sample. These wavelength excites electrons to permissible excitation states. When the electrons fall back to stable state, they emit photons. These photons are then collected by emission monochromator. The monochromator passes single emission wavelength which is further collected by detector which records PL spectra of sample. Figure 2.14 depicts working principle of PL spectroscopy.

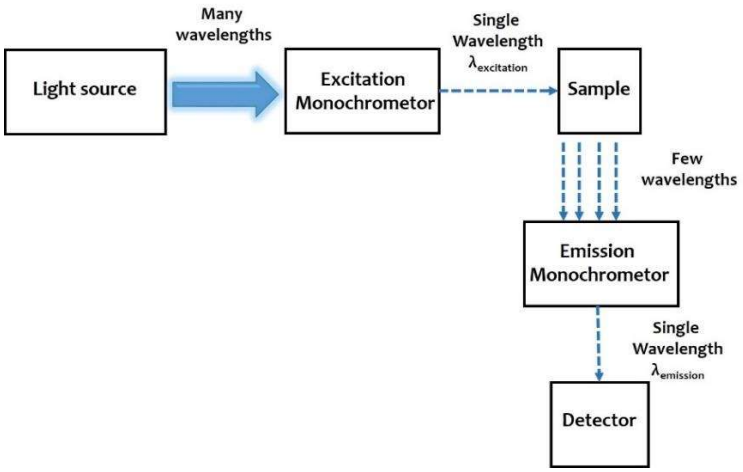

Figure 2.14: Working principle of PL spectroscopy

2.4.6 Raman Spectroscopy

Raman spectroscopy gives optical information which strongly depends on change in polarized properties of the material such as band gap and intrinsic defects present in material. When excitation laser falls upon sample and interact with molecule vibration. So recorded vibration modes gives complete information about band gap and intrinsic defects. Figure 2.15 shows schematic diagram of raman spectroscopy. In this process, system has an illuminating laser source which operates in visible, infrared and near infrared regions. These laser beams are focused on sample with the help of mirror assembly after which the scattered light passes through these focusing lenses and notch filter and are collected by spectrometer.

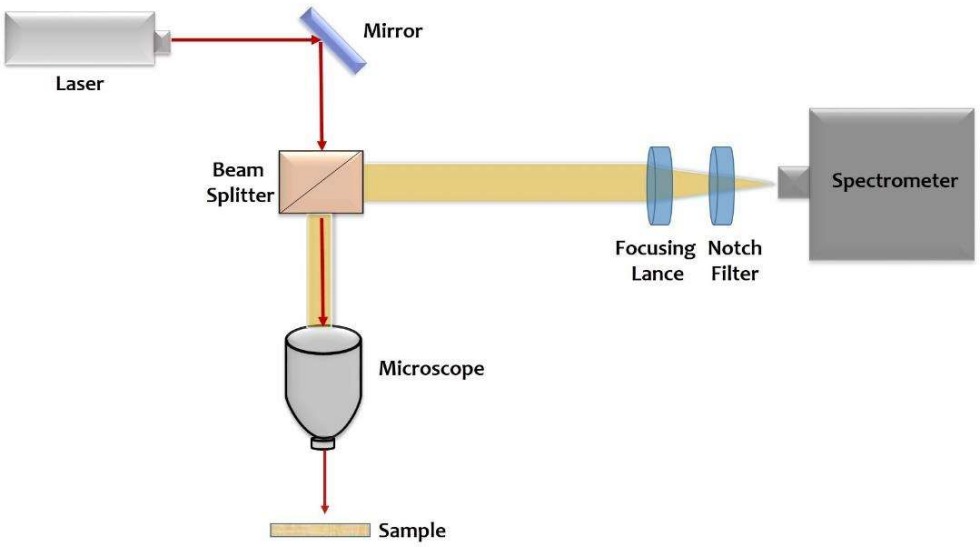

Figure 2.15: Schematic diagram of Raman spectroscopy

2.4.7 Electrical Characterization (I-V characterization)

The electrical characterization of semiconductor-semiconductor heterojunction or Schottky contacted heterojunctions were studied using I-V characterization. In this characterization two probe system is used for studying electrical properties of heterojunctions. Initially two probes were placed on metal contact with help of microscope on probe station. These probes were connected to Source meter (Keitheley-4200 SCS) which measure junction electrical properties in form of voltage sweep or current sweep. In voltage sweep in forward bias to reverse bias (-4 V to 4 V), source meter measure current in range of (10^{-6} A to 10^{-3} A). Using these current, heterojunction basic properties such as barrier height, ideality factor could be calculated. Figure 2.16 shows experimental setup for electrical characterization at IIT Jodhpur.

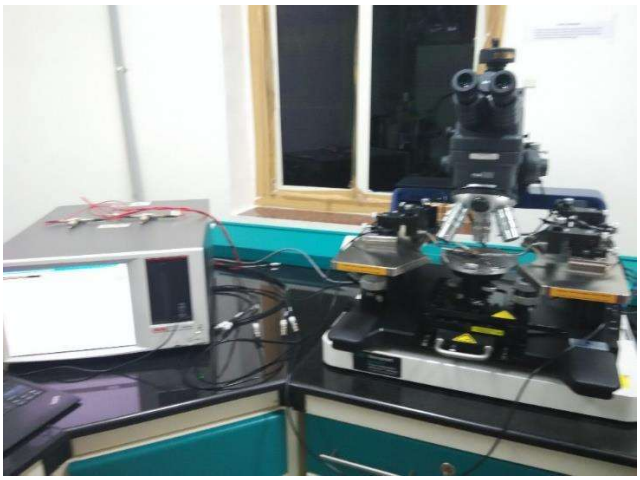

Figure 2.12: Experimental setup for electrical characterization at IIT Jodhpur

2.5 GAS SENSING CHARACTERIZATION

Gas sensing characterization system is optimized for various gases such as hydrogen detection (below its explosive limit~4%), CH_4, H_2S and CO_2 for that sensors relative response with response and recovery time recorded. For gas sensing chamber, customized stainless steel chamber (~8 liter volume) is used for gas sensing with gas fed through which isolated gas sensing chamber with external environments. Initially rotary pump is used to create vacuum (3×10^{-3}

mbar) to avoid environmental effects on gas sensing. There is four heating filament attached to external dc supply and could varied sensing platform temperature from RT to 200 °C which shown in PID controller. The operating temperature maintained constant during measurements which could be conformed using thermocouple. The sensing device mounted on platform where two probes with micromanipulator makes connection on sensors metal contacts in form of pressure contact. These two probes connected to source meter (keithley 4200-SCS) which recorded gas sensors response with time (sec). For 1% and 5% hydrogen in argon cylinders attached to gas sensing inlet port, sensors shows change in base line with respect to inflow of hydrogen gas concentration. For measuring hydrogen concentration in ppm level, two mass flow controller with 5 sccm gas flow attached to mixing chamber for achieving desired ppm hydrogen concentration level in to sensing chamber. Figure 2.17 shows customized gas sensing setup used at IIT Jodhpur.

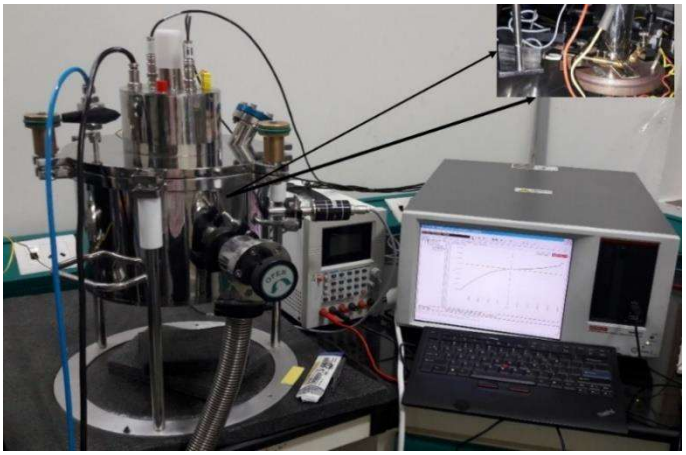

Figure 2.17: Customized gas sensing setup used at IIT Jodhpur

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