# Chapter 2

# Experimental Techniques

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This chapter provides detail of various characterization techniques and experimental details which have been part of the work in this thesis. The samples in the present study have been fabricated in thin film form using dc magnetron sputtering. The films compositions, film thickness, film surface roughness, crystal structures and magnetic properties of films were studied. Details of various characterization tools like energy dispersive X-ray spectroscopy (EDX), 3D optical profilometer, atomic force microscopy (AFM), X-ray diffraction (XRD), vibrating sample magnetometer (VSM) have been provided in this chapter.

## 2.1 Thin Film Growth: DC Magnetron Sputtering

Sputtering is the ejection of atoms by the bombardment of a solid target by energetic particles (ions), resulting from collisions between the incident energetic particles and surface atoms of the target [188–192]. The ions can be produced in two different way. First, by using an ion gun ions are produced which is directed towards the target material to be sputtered [191]. The second source of ions is a plasma which can be produced by introducing a gas in vacuum chamber of the sputtering unit under high negative voltage to the cathodes. The positive ions are accelerated from plasma by high electric field towards the cathode where target is placed and sputter the target atoms [192]. The second method is widely used in industries as well as in research works to deposit thin films. The sputtering technique can be done by two operations namely DC sputtering in which DC power supply is fed to the cathode, and the RF sputtering where AC power supply of radio-frequency is used.

DC magnetron sputter deposition technique is widely and most commonly used technique for deposition for thin films on various substrates. Sputtering technique works based on ion bombardment of target (source) material resulting atomic vapour of the target material which is then deposited on to the substrate. In magnetron sputtering technique, a magnetron source is used in which the bombardment of the target material by positive ions of the plasma is magnetically enhanced. The schematic a typical DC magnetron sputtering process is illustrated in the Figure 2.1.

In DC magnetron sputtering system permanent magnets are placed behind the cathode in suitable configuration. Cathode is connected to the negative terminal of DC power supply capable of supplying -2 to -3 kV. The target material to be deposited as thin film is placed at the cathode and substrate on to which the thin film is to be deposited is grounded. The substrate holder is equipped with heater that provides pre-substrate heating and in-situ annealing of the sample and an electric motor to provide substrate rotation for even deposition throughout the substrate. The chamber of the sputtering unit is equipped with rotary vane type vacuum pump for creating rough vacuum of order $10^{-2}$ mbar and diffusion pump or

turbomolecular pump for creating high vacuum pressure of order $10^{-5}$-$10^{-7}$ mbar. Due to high potential difference applied between the cathode and anode, Ar gas introduced inside the vacuum chamber get ionized (glow discharged) creating plasma where electrons and Ar+ ions are separated [189,190]. The electrons produced are influenced by the Lorentz force and execute helical motion towards the target and trapped in the region where electric field and magnetic field are perpendicular to each other above the target [190]. These electrons are capable of ionizing the Ar atoms. Thus ionization of Ar-gas is enhanced by the magnetron. Once ionization starts, Ar+ ions are accelerated toward the target attached to the cathode and bombard with the target and sputter the target material. The sputtered material are then transported to the substrate attached to the anode and thus thin film is sputter deposited. In our system, the DC magnetron sputtering system consists of four magnetrons and is capable of sputtering four targets at a time. The photos of DC magnetron sputtering system along with magnetrons and plasma glow during deposition of films are presented in Figure 2.2.

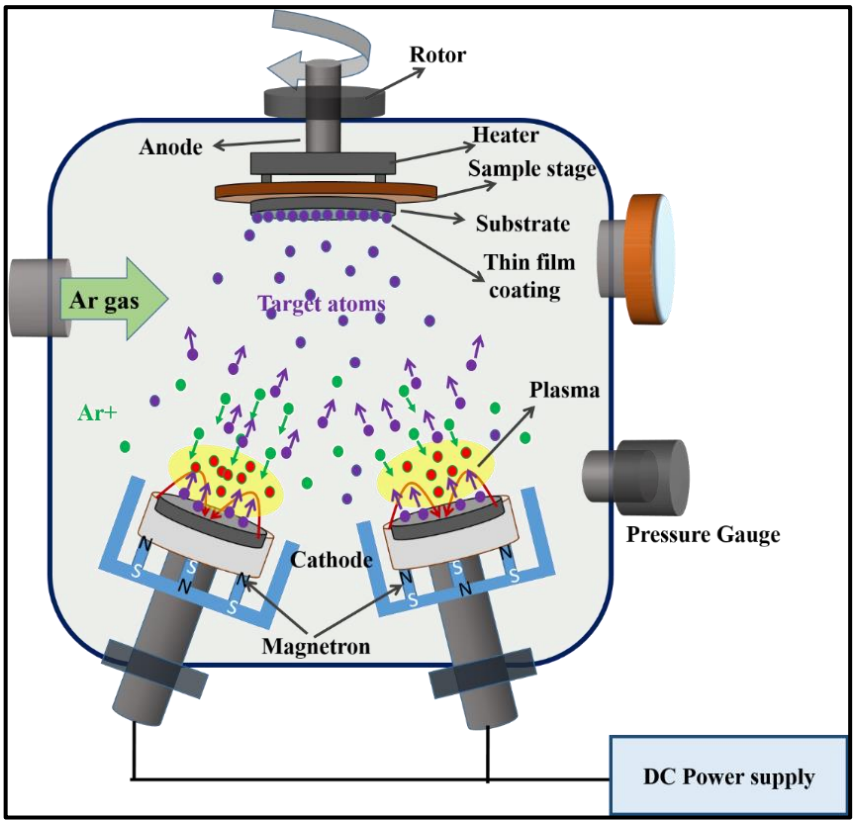


Figure 2.1 Schematic illustration of thin film growth by DC Magnetron Sputtering.

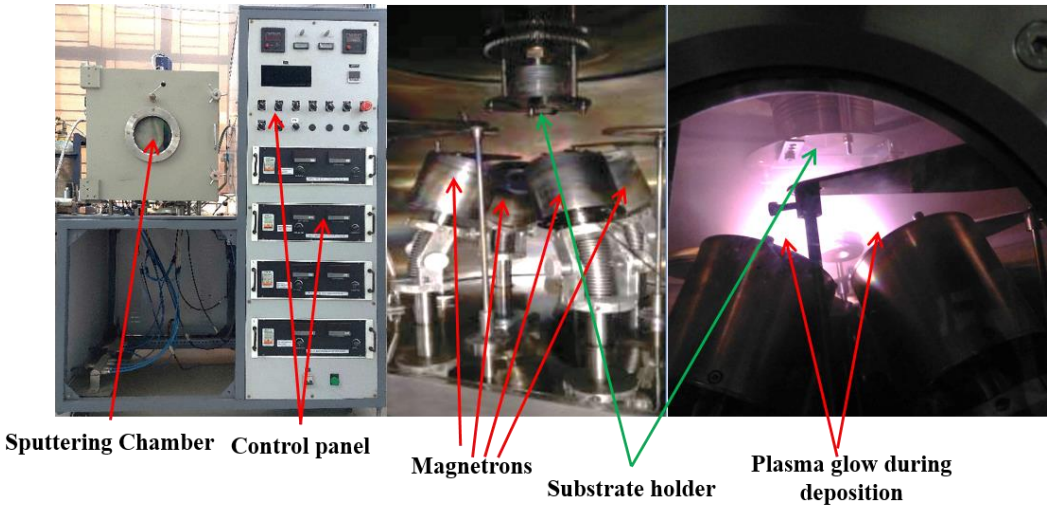


Figure 2.2 Photos of complete sputtering unit (left), magnetrons (middle) and plasma glow during deposition (right).

## 2.2 Study of Deposition Rate, Surface Roughness and Topography

### 2.2.1 3D Optical Profilometer

The 3D Optical Profilometer is a state-of-the-art profilometer for measurement of surface topography, step height and surface roughness of thin film using both white-light-interferometry (WLI) and phase-shifting-interferometry (PSI), which allows to produce high-quality surface profiles of sub-nanometer to millimeter level resolution with true-color images. The vertical resolution of the measurement is independent of the numerical aperture of the objective, enabling high-resolution measurements with a large field of view. The measured area can be further increased by stitching multiple fields of view into a single measurement. The two main parts of this optical profilometer are the detector and the sample stage. This profilometer is a non-contact optical profilometer that uses light instead of a physical probe. The key component to this technique is directing the light in such a way that the interference of the direct beam of light from source and reflected beam from the sample is reconstructed in 3D coloured surface. The schematic diagram of the instrumentation of 3D optical profilometer is illustrated in the Figure 2.3. In the current thesis work the Profilm3D Filmetrics Optical Profilometer is used. The Profilm3D uses white light interferometry (WLI) to measure surface profiles and

roughness down to 0.05µm along with phase shifting interferometry PSI option that can measure the minimum vertical feature size down to 0.001µm [193].

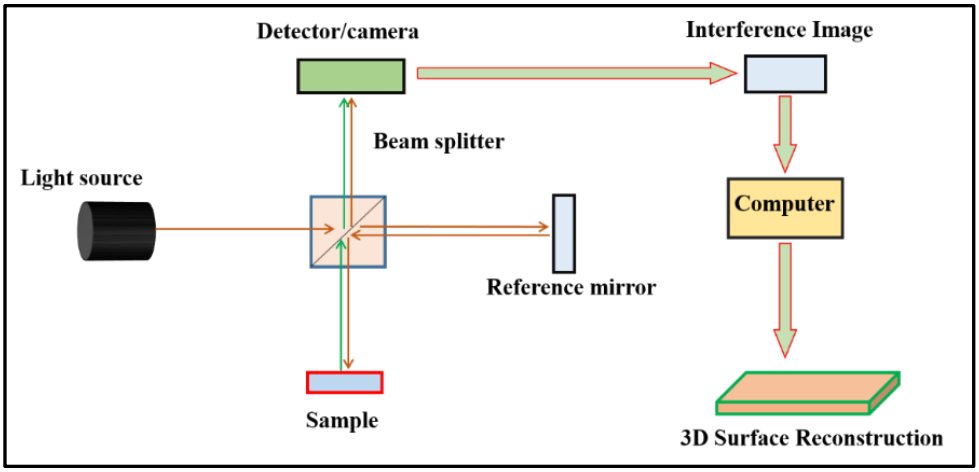


Figure 2.3 Schematic diagram of 3D imaging of surface topography of specimen by 3D optical profilometer.

## 2.2.2 Atomic Force Microscopy

Atomic force microscopy (AFM) is one of the versatile and powerful microscopy technique for the analysis of nanostructures and thin film surface profile. Atomic force microscope (AFM) was invented in 1986 by Gerd Binnig, Calvin F. Quate and Christopher Herber. It is useful in the imaging by plotting three-dimensional topography of the thin film and provides various types of surface measurements and height profile measurement at the atomic level. It is capable of generating images of very high resolution with minimum sample preparation efforts [194]. The basic components of AFM are displayed in Figure 2.4.

The working principle of AFM is based on the measurement of the interactive force between a tip and the sample surface using special probes made by an elastic cantilever with a sharp tip on the end. One end of the cantilever is firmly fixed on the holder, and the tip is located on the free cantilever end. The tip is made up of silicon nitride ($Si_3N_4$) and have average radius of curvature of 30 nm. The AFM is capable of operating in several modes including contact, tapping and non-contact mode. As the tip approaches the sample's surface, it is repelled by or attracted to the surface. The force between the tip and the sample (either attractive or repulsive) leads to deflection of the cantilever according to Hooke's law. The force applied to

the tip by the surface, results in bending of the cantilever. Measuring the cantilever deflection, it is possible to evaluate the tip–surface interactive force. A laser beam is used to detect cantilever movement towards or away from the surface depending on the force experienced. The reflected laser beam from the flat top of the cantilever, can detect slight changes in cantilever. A position-sensitive photo diode (PSPD) is used to track these changes. The cantilever tip passing over a raised and lowered features of surface of the specimen results in deflection of cantilever and causes subsequent change in direction of reflected beam is recorded by the PSPD. Using a feedback loop the height of the tip above the surface is controlled and maintaining constant laser position the AFM can generate an accurate topographic map of the surface features [195–197]. The scanning of the sample surface can be done in various modes (a) contact mode in which the tip comes in contact with the specimen surface, (b) non-contact mode, in which the tip of the scanning probe does not come in contact with the surface of the specimen and (c) tapping mode: in tapping mode the tip of the scanning probe intermittently make contact over the surface of specimen. The AFM model: Innova, Make: Bruker has been used in the current thesis work for characterizing film surface topography and film surface roughness.

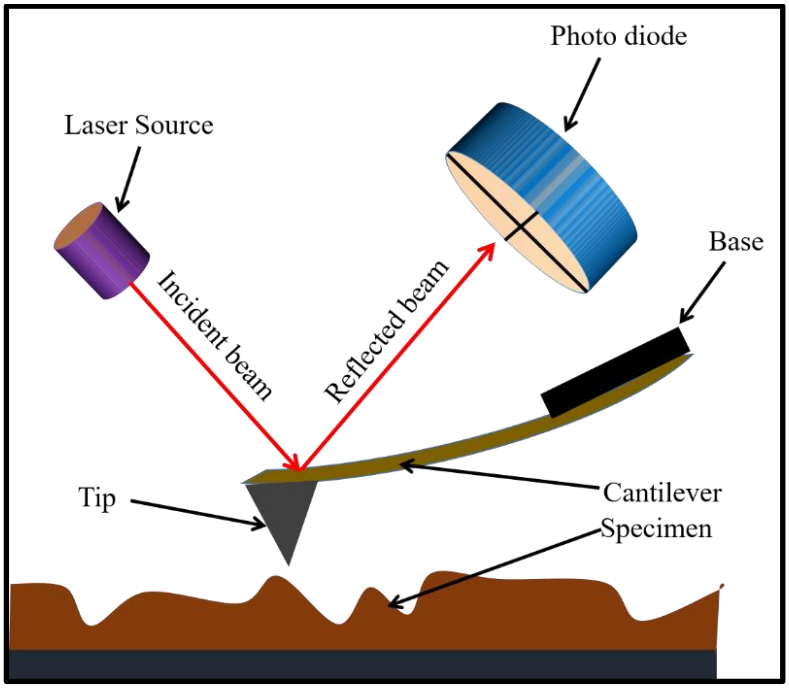


Figure 2.4 Schematic diagram of imaging of Atomic Force Microscopy.

## 2.3 Field Emission Scanning Electron Microscopy

The FE-SEM is one of the most widely used instruments in material research. This is used to characterize surface morphology and topography, composition and other properties of specimen. The schematic illustration of FE-SEM is presented in Figure 2.5. A beam of electrons is produced by the Electron gun and accelerated by accelerating anode using a positive electric potential and directed towards the specimen. The electron beam is then confined and focused using magnetic lenses into a thin focused monochromatic electron beam. Electrons in the beam upon incident on the specimen surface interact with atoms of the specimen and produces (a) secondary electrons (b) backscattered electrons (c) auger electrons (d) X-rays etc. The secondary electrons emitted from the specimen surface are highly surface specific and are emitted from a depth of <=20 Å. Due to lower energy of secondary electrons (energy<50 eV), they are extremely abundant and their outcome is dependent on the accelerating voltage. The backscattered electrons (energy>50 eV) are generated by elastic scattering of incident electron beam and the yield depends on atomic number Z of the specimen [198–200] and thus gives information from relatively deep region of specimen. So this feature is used to observe topography, or Z-contrast of specimen surface. These interactions and effects are detected and transformed into a three dimensional image.

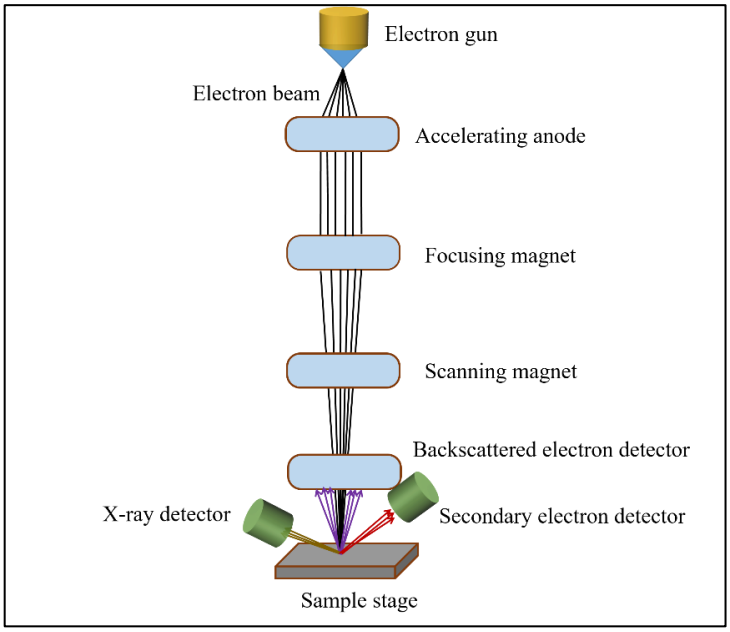


Figure 2.5 Schematic block diagram of a typical FESEM.

## 2.4 Energy Dispersive X-ray Spectroscopy

Energy Dispersive Spectroscopy (EDS) also termed as energy dispersive X-ray spectroscopy (EDX) is a useful elemental analysis technique used for determining the elemental composition present in the given sample in powder or thin film form. In EDS analysis the sample is irradiated with energetic electron beam and K-electrons bound to nucleus of the sample is knocked off creating a hole. This hole is filled by the transition of electron from higher energy shell by emitting characteristic x-rays which are element specific. The characteristic X-rays provide the qualitative information about the elements present in the sample. The basic principle of characteristic X-ray generation is illustrated in the Figure 2.6. The EDS instrumentation generally comes as an accessory with SEM or TEM. It consists of an electron gun, X-ray detector and software to analyze energy spectra. The electron gun produces high energy electron beam which are directed to the sample. Electron beam upon incident on the specimen surface various interactions as depicted in Figure 2.7 takes place. The X-ray emitted by the sample is absorbed by the detector and converted to an electrical signal and digital image and displayed on the computer screen. This electrical signal gives the useful information on sample's elemental composition.

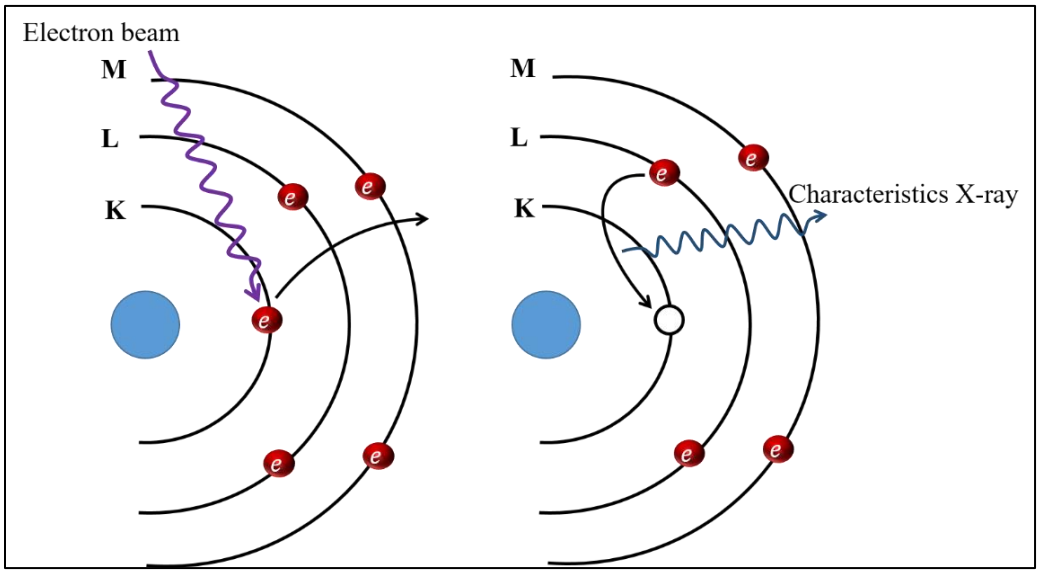


Figure 2.6 Basic principle of characteristic X-ray generation. (Left) The K-electron is knocked out by incident electron beam. (Right) The electron vacancy in K-shell is filled by electron of higher energy shell by emitting energy in the form of characteristics X-ray.

In this thesis work, the Field Emission Scanning Electron Microscope (FESEM) with OXFORD EDS, Make: Zeiss, Model: Sigma and SEM equipped with EDS make: JEOL JAPAN, Model: JSM 6390LV were used.

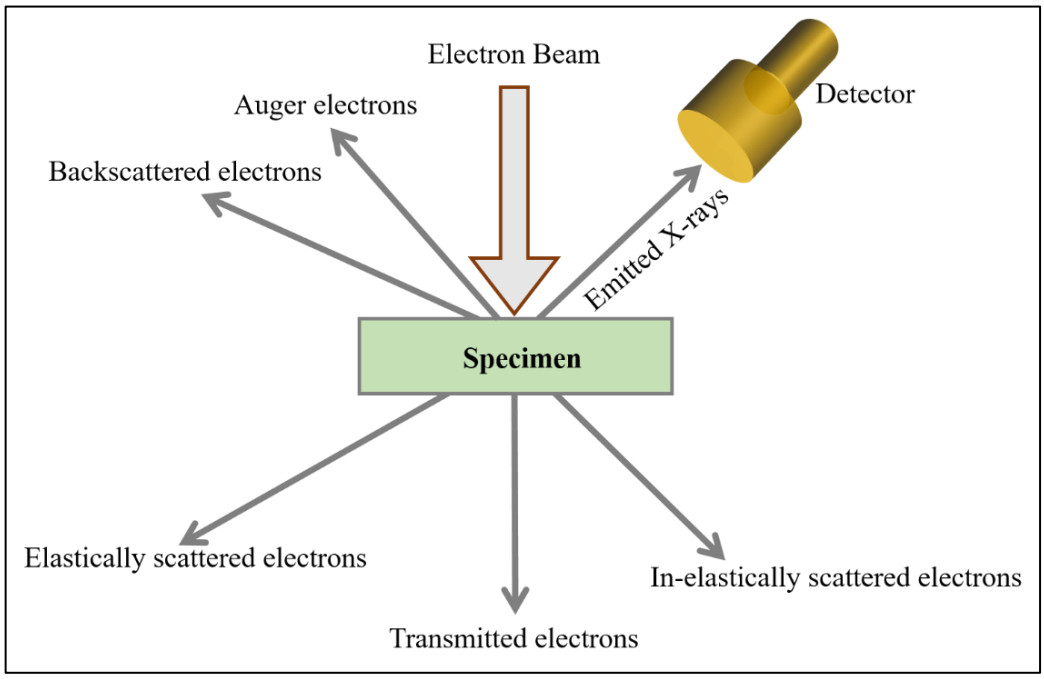


Figure 2.7 Schematic diagram of EDS detection scheme.

## 2.5 Structural Characterization by X-ray Diffraction

X-ray diffraction technique is a rapid analytical technique primarily used for structural analysis and phase identification of the crystalline materials for both powder and thin film sample. The x-ray diffraction from a sample can provide various information such as crystal structure, unit cell parameters, crystallite size, strain etc. Max von Laue discovered (in 1912) that crystalline substance can act as three dimensional diffraction gratings for X-rays whose wavelength is of the order of crystal lattice plane spacing [201]. X-ray diffraction is based on the principle of constructive interference of monochromatic X-rays diffracted by atoms present in the planes of crystal lattice. The interaction of incident X-rays with the sample produces constructive interference when Bragg's law- $2d_{hkl}\ sin\theta = n\lambda$ is satisfied (Figure 2.8) [21,201,202]. This law relates the wavelength $\lambda$ of electromagnetic radiation (X-ray) with diffraction angle ($\theta$) and spacing ($d$) of ($hkl$) planes of crystal

lattice of the sample. X-ray diffraction has now become a common technique for routine study of crystal structures and atomic spacing. This technique is now commonly used for phase identification of sample, calculations of unit cell parameters and also crystallite size.

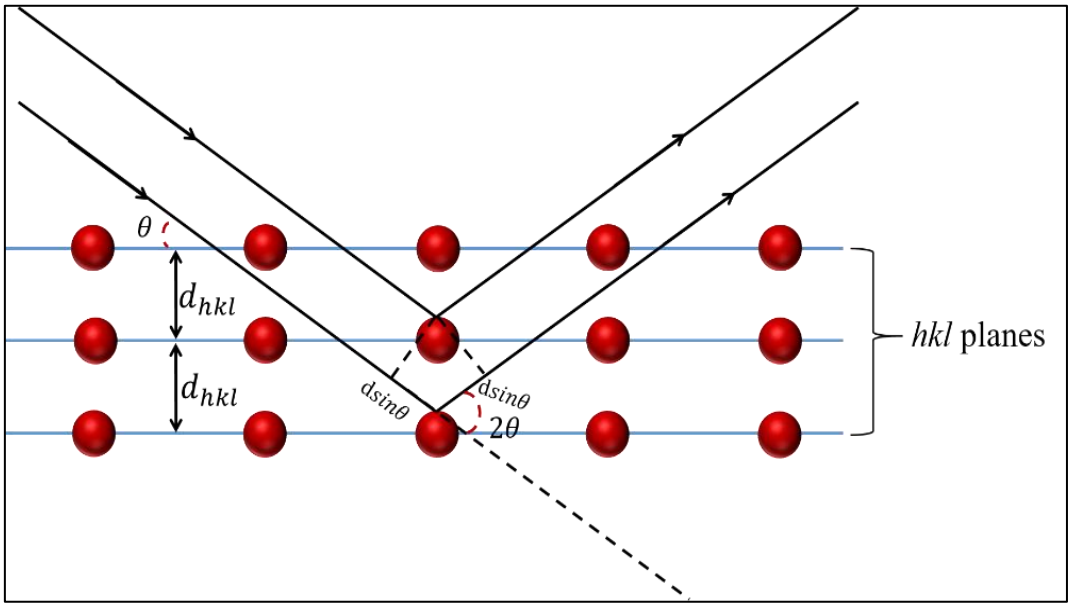


Figure 2.8 X-ray diffraction by atoms of different crystal planes.

The X-rays generated in the X-ray tube are filtered and monochromatic X-rays are directed to the sample, and diffracted X-rays are collected in the detector. The basic elements of a typical X-ray Diffractometer are: X-ray tube, goniometer, X-ray detector and electronics for counting detector pulses. The schematic diagram of typical X-ray diffractometer is shown in the Figure 2.9. The specimen is supported on a sample holder. The X-rays emitted from the source fall on the specimen and diffracted by the specimen. The diffracted beam pass through the focusing slits and then enters the detector. The receiving slits and detector are supported on the carriage, which can be rotated in a circular path such that the detector is always at 2theta position with respect to the incident X-rays [201,203].

In the present thesis work, we have used two XRDs, Bruker AXS, D8 Advance and Grazing incidence x-ray diffraction (GIXRD) Make: Rigaku corporation Japan, Model: SmartLab.

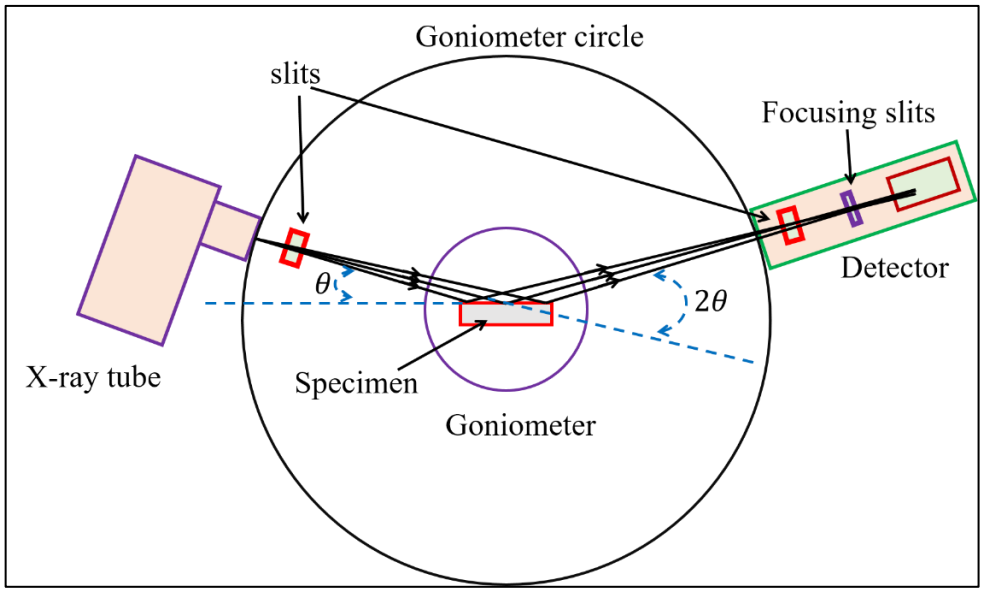


Figure 2.9 Schematic diagram of a typical X-ray diffractometer.

## 2.6 Magnetic Characterization

### 2.6.1 Vibrating Sample Magnetometer

The magnetic moment per unit volume resulting from either motion of electrons in atoms or the spin of electrons in the atoms of a material is known as magnetization. The net magnetization results from the response of a material to the external magnetic field as well as from the unbalanced magnetic dipole moment that may be inherent in the material itself. The magnetization of a material varies under the influence of external magnetic field as well as temperature. Upon application of external magnetic field, magnetic moments of a material align in the direction of applied field, and the net magnetization increases with increase in the applied magnetic field. On the other hand, with increase in temperature, the atomic magnetic moments flip in random directions due to thermal energy, and hence the net magnetization of material decreases. Thus the measurement of magnetization can be done in two different ways- (a) measurement of magnetic moment with change in applied magnetic field at constant temperature and (b) measurement of magnetic moment with change in temperature at low applied field. In low applied field we have magnetic susceptibility and in high applied field we have induced magnetization.

The magnetic moment can be measured in three different methods (a) by measuring force on the magnetic material in a nonuniform magnetic field, (b) by measuring the magnetic induction in the vicinity of the sample and (c) indirect measurement of phenomena which involve magnetic properties [203–206]. VSM works on the principle of Faraday's law [207,208] of induction, which tells that the changing magnetic field produces an electric field. This electric field in turn can be measured and provides the information about the magnetic moment of the sample with changing magnetic field or temperature. In a typical VSM system the sample is made to vibrate perpendicularly to the applied field. The oscillating magnetic field of the vibrating sample induces a voltage in the pickup coils. From measurement of this voltage the magnetic moment of the sample are deduced as a function of applied magnetic field or as a function of temperature. The VSM a versatile magnetometer which is sensitive to measure weak signal of $10^{-7}$ to $10^{-9}$ emu [205]. Schematic block diagram of a typical VSM is depicted in Figure 2.10.

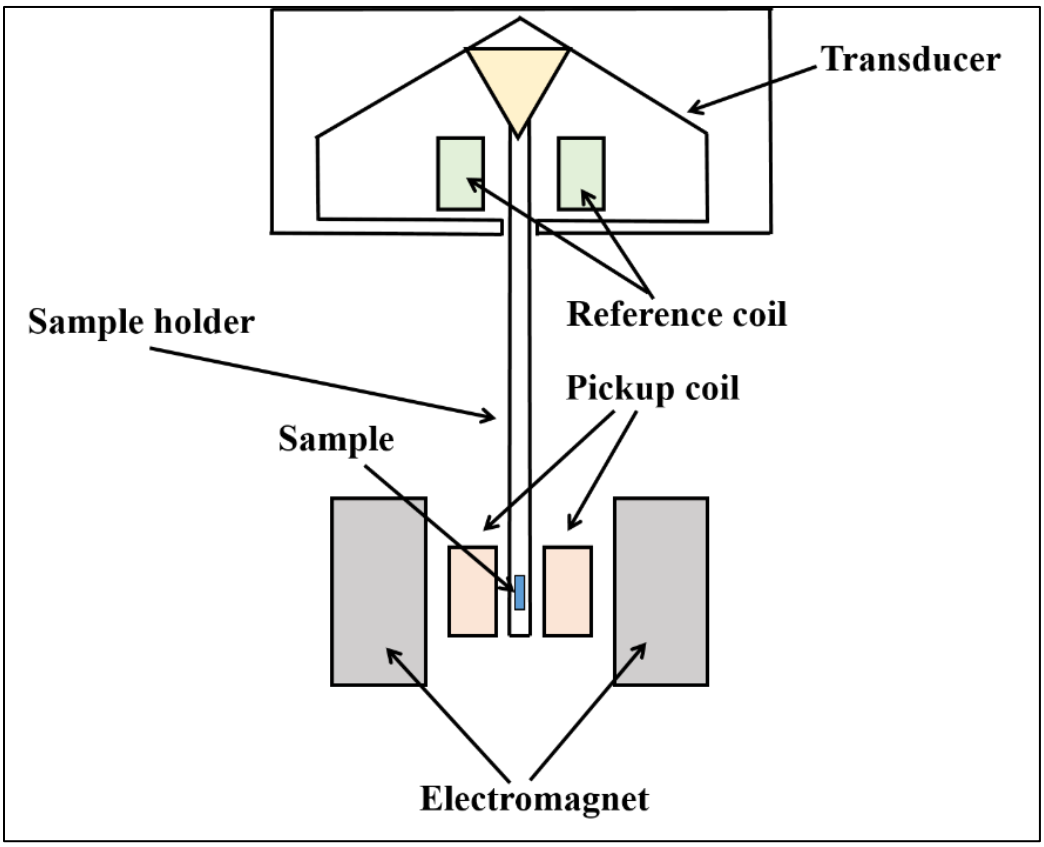


Figure 2.10 Schematic block diagram of a typical VSM.

VSM is used for the measurement of the magnetic properties of materials in powdered, thin films and for study of GMR, CMR, TMS etc. and other magneto-optical properties. In the present thesis work the magnetic (M-H) measurements were carried out using two different VSMs, one Lakeshore 7400 series, and the other Make: MicroSense VSM, USA, Model: EZ16.

### 2.6.2 SQUID Magnetometer

Superconducting Quantum Interference Device is the most sensitive device used today for the detection of magnetic moment up to the sensitivity limit of $10^{-8}$ emu. SQUIDs are used in wide range of applications such as nuclear magnetic resonance (NMR), susceptometry, non-destructive evaluation, biomagnetism, scanning SQUID microscopy, magnetic moment measurement etc. The magnetometer consists of three major components, the pick-up coils, flux transformer and SQUID (Superconducting Quantum Interference Device). All these components are enclosed under a superconducting shield. The schematic block diagram of SQUID magnetometer is presented in the Figure 2.11. The sample is mounted on a non-magnetic sample holder and lowered into the magnetometer's sense region, and a dc current is initiated by pickup coils in its superconducting circuitry. This current is fed to another coil via flux transformer where it is amplified and detected by SQUID. The SQUID then functions as an extremely sensitive current to voltage converter, outputting the change in magnetic flux measured by the pickup coils as a dipole voltage response. When calibrated to a sample of known mass, magnetic moment of the sample can be obtained in electromagnetic units (emu). The sensitivity of SQUID is such that it can measure the signal of $5x10^{-8}$ emu [209]. By this system magnetization can be measured as a function of temperature over a temperature range of (2-400) K.

The SQUID consists of two superconducting ring separated by two insulating layers to form one (in rf SQUID) or two (in dc SQUID) parallel Josephson junctions. The basic phenomena which governs the operation of SQUID is quantization of magnetic flux in superconducting ring. Flux quantization refers to the fact that the

total magnetic flux in the superconducting loop is always an integral multiple of quantum flux expressed by relation [210],

$$\emptyset_{tot} = \emptyset_{ext} - LI_S = n\emptyset_O$$

Where $\emptyset_{ext}$= external applied field, L=self-inductance of superconducting ring, Is= screening current, n=an integer and $\emptyset_O$= quantum flux.

The SQUID magnetometer can detect sufficiently small magnetic fields which is enough to measure the magnetic field in living organisms such as magnetic field produced by human brain. The dc-susceptibility measurements record the equilibrium for the magnetization while ac-susceptibility measurement yields the information about the magnetization dynamics in a material. For ac- susceptibility measurement, a small ac drive magnetic field $H_{ac}$ with frequency $\omega$ is applied to the sample in addition to any larger applied dc field inducing a time dependent moment. The ac-susceptibility is defined as $\chi_{ac}$ = dM/dH. Thus small changes in the magnetization behavior can be detected. The ac susceptibility can be interpreted in two components, the real and the imaginary part which probe dM/dH and dissipative processes in the sample respectively [209].

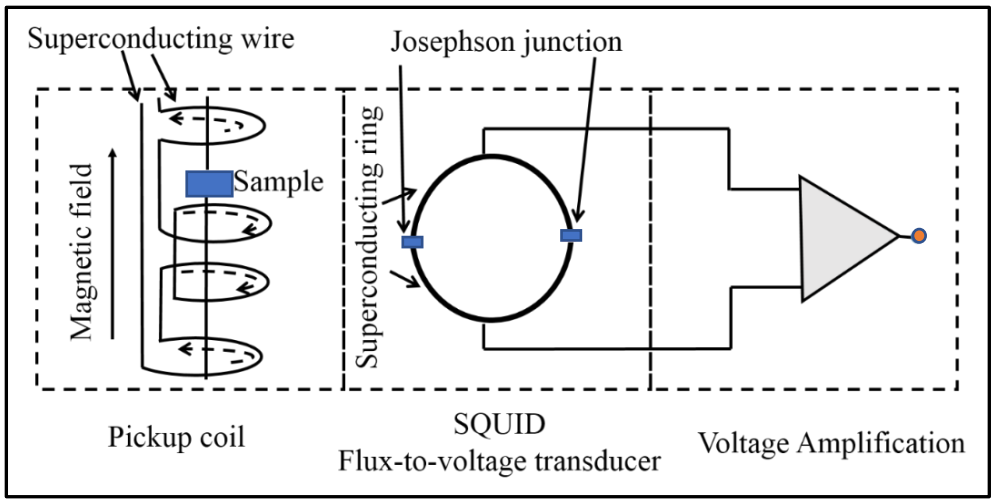


Figure 2.11 Schematic diagram of quantum design magnetometer.