3. Experimental

3.1. General description of apparatus used

3.1.1. Hot plate magnetic stirrer

A hot plate magnetic stirrer was employed to stir the solution for deposition of PVDF thin film and also ZnO solution to obtain it in powder form. Stirring rate of the stirrer can also be controlled to achieve solution in desirable form. It is combined with temperature controlling system so that suitable temperature for solution preparation can be provided.

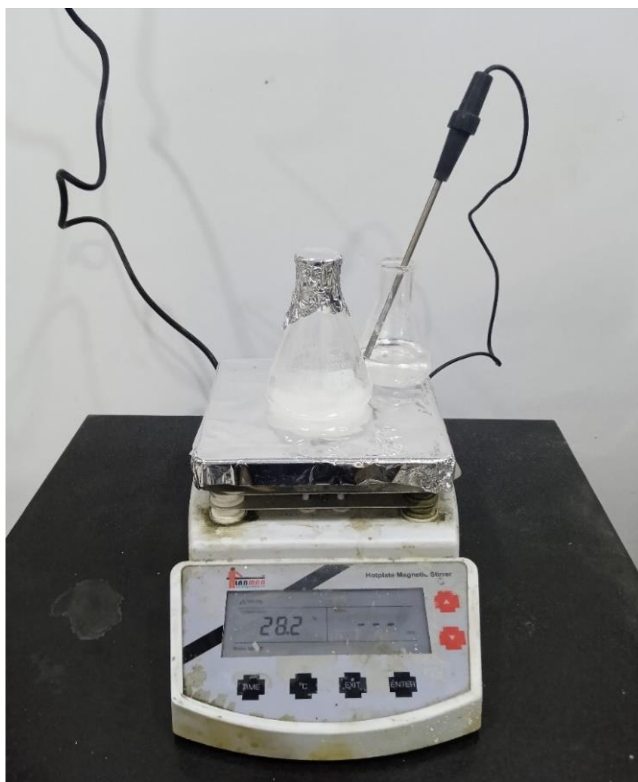

Fig. 3.1 Picture of hot-plate magnetic stirrer

3.1.2. Ultrasonic cleaner

An ultrasonic cleaner is an instrument which produces ultrasounds up to frequency of 40 kHz. Inside the bath some liquid is placed which is agitated by the generated ultrasound. The bath is usually filled by water or any other cleaning liquid. An ultrasonic cleaner (from UR Biocoction) has been utilized in cleaning process of the substrates before deposition of film on it. It has been widely employed in blending of materials in solution form and also well dispersal of nanoparticles. They are also used in removal of external contamination from the surface of substrates. It also provides an adjustable digital timer with temperature sensing capability for better convenience.

Fig. 3.2 Picture of ultrasonic cleaner

3.1.3. Spin-coater

A manually programmable spin-coater (spin NXG-M1) from Apex instruments has been utilized in synthesis of thin films on substrates. This instrument helps us to produce thin coating of materials on flat substrates. Solution of any material is deposited onto the substrate which spun off at a high velocity up to 8000 rpm to synthesize a thin uniform layer. Angular speed helps in determining thickness of those deposited films.

Fig. 3.3 Picture of manually programmable spin-coater

3.1.4. Hot air oven

A hot air oven (UR Biocoction) has been employed in drying process. This equipment is designed to provide particle free air inside the oven. It is capable of providing accurate

temperature environment in the range of 5 ^{0}C – 250 ^{0}C. The instrument is very accurate in providing temperature with error $\pm$ 1 ^{0}C. It can produce temperature with a resolution of 0.1 ^{0}C. It has been used during cleaning process of substrates. To remove unwanted dust or dirt from substrate surface, after washing it by soap solution, distilled water and finally isopropanol they have been placed in the air oven for quick drying. Also after spin coating process, synthesized films have been placed in it in order to remove unwanted compounds that were added through precursor solution mixture. So placing those films at a particular temperature for a specific period of time plays a crucial role in growth mechanism of those synthesized films.

Fig. 3.4 Picture of hot air oven

3.1.5. Sourcemeter

Kiethley model 2450 sourcemeter instrument is the instrument with combined facilities of multimeter, power supply, current source and electronic load. It can precisely measure source voltage and current simultaneously. It is considered to be a better equipment compared to any of those due to its versatility and high accuracy. This type of device is capable of sourcing and measuring at the same time. It has a high-resolution 5 inch touch-screen display with enhanced graphical data visualization. It is able to perform sensitive measurements even at low level signals. It also possesses source-meter sweep capabilities in linear and logarithmic steps. High capacitance mode is also present for load impedance up to 50 µF. This instrument filters to reduce the noise signal during measurement. It is also protected from overcurrent or overvoltage through rear-panel connector.

Fig. 3.5 Picture of source measure unit (SMU)

3.1.6. UV-VIS-NIR spectrophotometer

A UV-VIS-NIR spectrophotometer (from Ocean Optics) is utilized to measure the optical properties of synthesized materials in thin film form. This instrument directly provides

transmittance, absorbance or reflectance spectra of any material in the wavelength range of 200 – 900 nm. It records the spectral transmittance for each wavelength by comparing the transmitted radiation to the incident radiation. It consists of two segments, a spectrometer and a photometer. Spectrometer emits a spectrum of light while photometer measures the amount of light after passing through the sample. A basic spectrophotometer instrument consists of a broad band light source, monochromator, wavelength selector, collimator, Photodetector and sample holder.

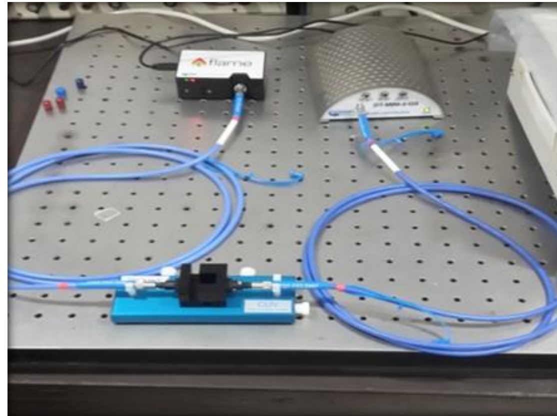

Fig. 3.6 Picture of UV-VIS spectrophotometer

To measure the absorbance spectrum, a beam of light is passed through the sample. The light source emits light, which entering upon the monochromator splits into a spectrum of different wavelengths. Each of the selected wavelengths are allowed to pass through the sample through reference a path. The two light beams, the transmitted one and the original beam converge at the detector. The ratio of their relative intensities gives measure of transmittance or absorbance. Absorption coefficient of the sample is measured from transmittance data using the relation

$$\alpha = \log_{10}(100/T)/d$$

Where T is percentage of transmittance and d is thickness of the sample through which incident light has traversed. From this obtained absorption data band gap of the sample can be estimated from Tauc plot using the following relations

$$(\alpha h\nu)^2 = c(h\nu\text{-}Eg) \quad \text{for Direct allowed transitions}$$

$$(\alpha h\nu)^{1/2} = c(h\nu\text{-}Eg) \quad \text{for Indirect allowed transitions}$$

Band gaps of those materials can be determined by extrapolation of the linear portion of these curves to energy axis.

3.1.7. Scanning electron microscope (SEM)

As dimension of materials shrinks, they are not visible by ordinary light microscopy. A scanning electron microscope (SEM) is generally used to create image of a surface which human eye can’t resolve. It has many useful facilities like higher magnification, depth of focus, better resolution over ordinary light microscope. An SEM usually consists of source of electrons, sample chamber, column through which electrons travel with electromagnetic lenses, electron detector after diffraction and computer display to view the images. It consists of a tungsten filament which acts as cathode generates electrons by thermionic emission. There is an anode kept at positive potential with respect to cathode to accelerate those electrons. These produced electrons are passed through combination of electromagnetic lenses to produce focused beam of electrons which can now hit the surface of the sample. The sample is placed on a mounted stage inside the vacuum chamber which is evacuated by pumps earlier. The position of electron beam on the sample surface is controlled by some scan coils situated above the lenses. This scanning of beam enables to gather information about that scanned surface area. This beam of electrons interacts with the sample surface to produce information about the morphology of that surface or composition of the material. The beam of electrons produces some primary electrons scattered from the sample surface, secondary electrons and are collected by the detector. Samples are coated by a thin layer of heavy metal for transfer of electrons from sample surface producing images with better clarity. Imaging of the surface is being performed by collecting beam of electrons over a section of area. In addition to these primary scattered electrons, there will be some additional secondary emitted electrons collected by the detector. After reaching the collector these secondary electrons strike a luminescent material which generates light flashes. These light flashes is then converted into electrical signal by photo-multiplier tube which sends a signal to cathode ray tube and produces high resolution image of the sample surface. The number of secondary electrons that enters the

detector surface determines the surface morphology of the sample. Raised surfaces produces more number of secondary electrons compared to that of depressed surfaces. So raised surfaces will be looking brighter in the screen compared to that of depressed surfaces. Schematic representation of scanning electron microscopy and picture of the instrument are shown in fig. 3.7 and fig. 3.8 respectively.

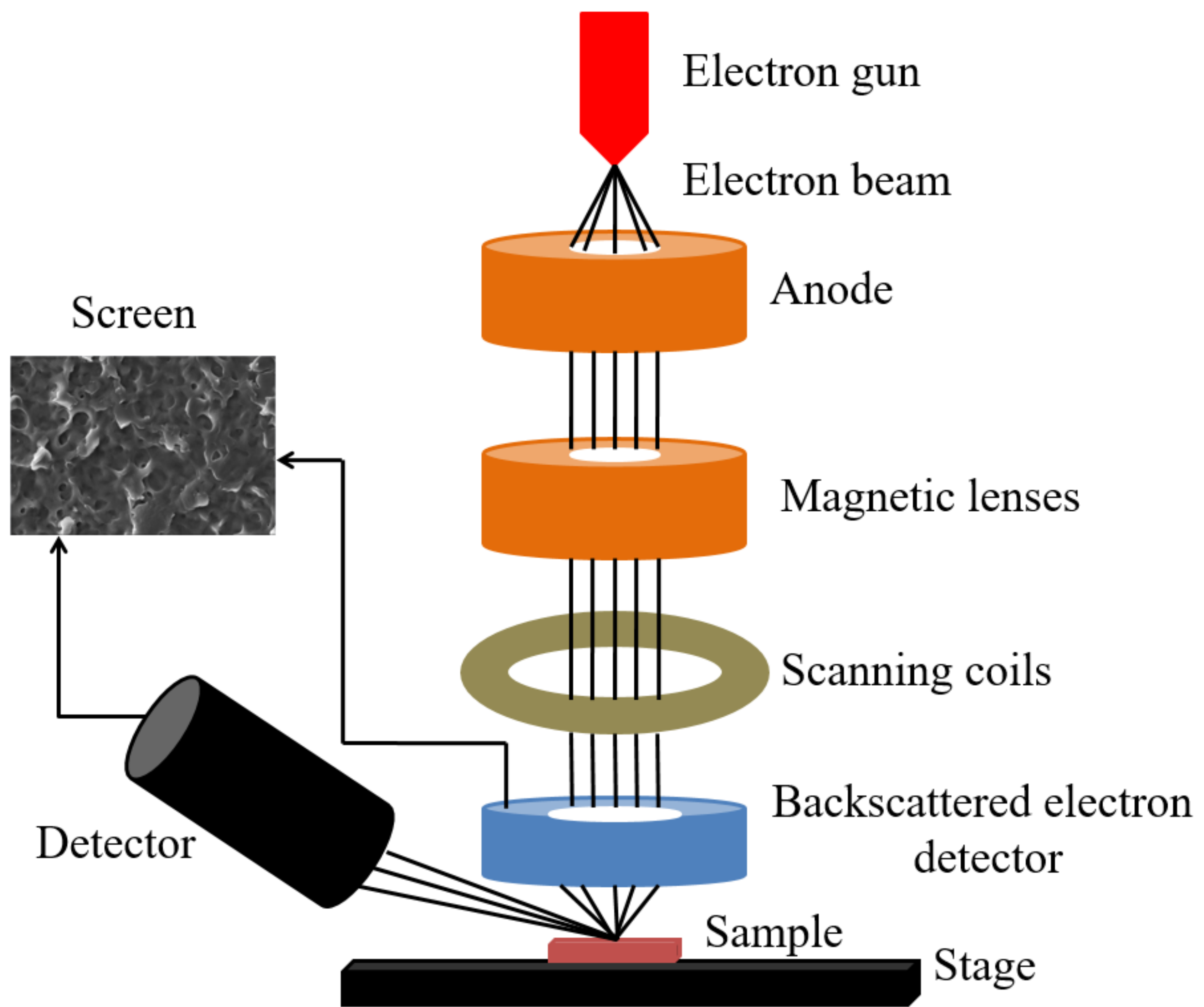

Fig. 3.7 Schematic representation of scanning electron microscopy

Fig. 3.8 Picture of scanning electron microscope (SEM)

3.1.8. X-ray diffractometer (XRD)

An X-ray diffractometer or XRD is an instrument used in analyzing and determination in structure of materials from the scattering pattern. XRD works on the principle of Bragg's law. It is based on wide angle elastic scattering of X-ray beam preferably from ordered material surface to produce a constructive interference pattern of monochromatic X-rays. This X-ray is produced in a cathode ray tube which is later filtered to produce monochromatic radiation. To produce X-rays, at first a filament is heated to liberate electrons from it. These electrons are then accelerated by applying voltage. These high energy electrons are then used to bombard the target material. Different target materials like Cu, Fe, Mo, Cr give rise to distinct wavelengths. But Cu is the most common target material which emits characteristic X-ray with CuK_{α} line of wavelength 1.54 Å. When these high energetic electrons dislodge inner shell electrons from the target material, characteristic X-ray is produced. These X-rays are then

filtered by crystal monochromators to generate radiation of specific wavelength so that interference pattern can be produced. Then this radiation is concentrated and collimated before incident on the sample. The detector is then rotated at different angles to record the intensity pattern of the reflected beam from the sample. The pattern shows some peak after reflection from the sample surface due to constructive interference satisfying the relation $2d_{hkl}\sin\theta = n\lambda$. Where $d_{hkl}$is the spacing between the crystal planes, λ is the wavelength of incident X-ray, θ is the angle of reflection from the lattice planes and n representing integer numbers. $2d_{hkl}\sin\theta$ is the path difference between those X-rays reflected from consecutive lattice planes. For particular θ values, when path difference is integral multiple of wavelength of incident X-ray, constructive interference occurs. This generated pattern allows identifying different elements as well as structure and crystallite size. These obtained results are then compared with JCPDS data for known crystal structures for identification of crystal phases. Different h, k, l values are assigned to different peaks and are used to calculate lattice parameters. Lattice parameters (a, b, c) are related with inter planner spacing d_{hkl} by Miller indices following the relation

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2+\left(\frac{k}{b}\right)^2+\left(\frac{l}{c}\right)^2}}$$

For a simple cubic lattice a=b=c and the relation reduces into a simpler one

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}}$$

While recording the intensity pattern of diffracted X-ray, the detector and the sample is rotated through their respective axes. Intensity pattern shows some kind of peaks when particular d spacing of crystal for an angle θ matches with path difference of reflected rays from adjacent crystal planes. Results are presented in form of some peaks in intensity distribution in different 2θ positions.

We have utilized an X-ray diffractometer (PANalyticalX'Pert Pro) with characteristic X-ray beam of CuK_α line (λ=1.54 Å) for characterization of synthesized materials as shown in fig. 3.9.

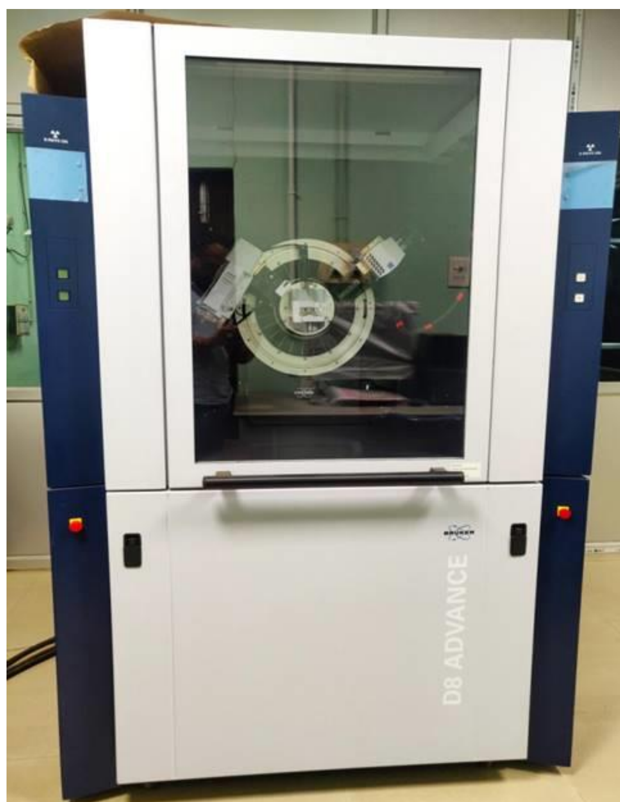

Fig. 3.9 Picture of X-ray diffraction (XRD) instrument

3.1.9. Fourier transformed infrared (FTIR) spectrometer

Infrared (IR) is a portion of electromagnetic (EM) spectrum very useful for the analysis of various organic compounds because of their molecular environment. IR radiation has wavelength ranging from 700 - 1000 nm. IR spectroscopy is based on the interaction of IR radiation with matter. The goal of any spectroscopy is to measure how much light is absorbed by any sample while passing through it for each wavelength. IR radiation of specific photon energy is absorbed by materials depending upon the bonds and their constituting atoms. This IR radiation excites covalently bonded atoms to individual vibrational energy levels. But in Fourier transformed infrared (FTIR) spectroscopy, we obtain raw absorption spectrum from an interferogram as function of mirror position of the interferometer. So to obtain absorption spectrum in wavenumber domain, acquired data should be Fourier transformed. An FTIR spectrometer generates high-

resolution spectral data over a broad range of spectrum. FTIR method has an advantage over other spectroscopy technique, since incident spectrum is very precisely calibrated to laser so that it has superior signal to noise ratio. An FTIR consists of an IR source, half silvered mirror used as beam splitter, two reflecting mirrors, laser source and detector as shown schematically in fig. 3.10. The emitted IR radiation from a glowing source falls on a half silvered mirror after passing through an aperture to control intensity of the beam. In FTIR instrument the mirror is situated at an angle of 45^0 to the incident beam. After incidence on the beam splitter it gets partially reflected and partially transmitted. These rays are incident on two mirrors one of which is movable and the other one is fixed. The moving mirror's position is determined depending upon calibrating laser's response. These two split beams again unify at the beam splitter to produce an interference pattern depending upon their path difference. This emerged beam is then passed through the sample material. The emerged signal after absorption from the sample is now Fourier transformed to obtain it as function of wavenumber. Since information for all wavelengths is gathered at once, signal to noise ratio is also reduced in the absorption spectrum.

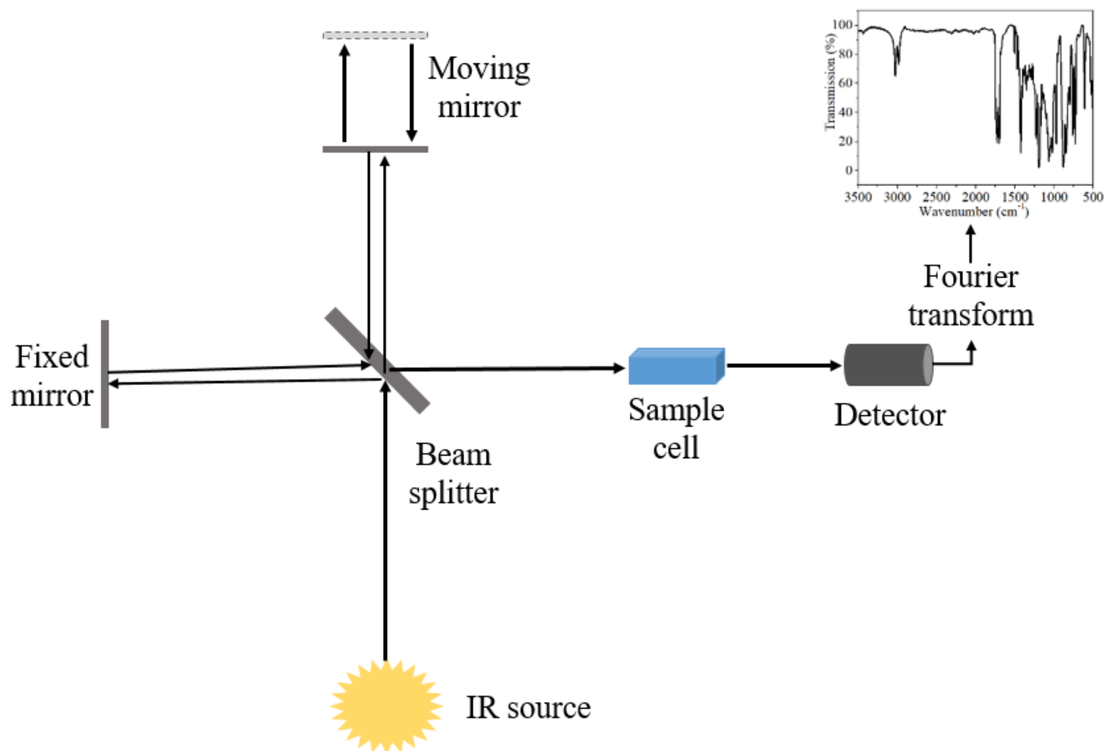

Fig. 3.10 Schematic representation of FTIR spectroscopy

3.1.10. X-ray photoelectron spectrometer (XPS)

X-ray photoelectron spectroscopy (XPS) is method based on photoelectric effect used to identify composition of any material. Actually it is based on the principle of photoelectric effect where electrons are emitted due to incidence of electromagnetic radiation. An XPS instrument consists of ultrahigh vacuum system, X-ray source, ion gun, charge neutralizer, electron energy analyzer, computer and analyzing software as shown in fig. 3.11. The entire experiment is performed inside a vacuum chamber operating typically at $< 10^{-9}$ Torr. This is required so that emitted electrons with relatively low energy do not get absorbed at the ambient atmosphere and ejected electrons don't lose their kinetic energy. Inside the chamber there is an X-ray source typically emits Al K_α or Mg K_α lines. A monochromator is used to allow X-rays with desirable energy to target the sample. The electron analyzer in form of concentric hemispherical analyzer is then used to measure kinetic energies of those produced photoelectrons. Usually an ion gun is used to sputter the sample surface for charge neutralization and to get rid of environmental contaminants. This electron energy analyzer produces a spectrum of intensity of ejected electrons with their binding energy. Each intensity peak at a particular binding energy represents a particular element. Apart from identifying elements from the sample, they can also specify fraction of elements present there depending upon the intensity. Intensity of those peaks corresponds to number of particular atoms present there in that sample.

In analysis of XPS spectra, the peak position along the X-axis indicates elemental and chemical composition of material. The X-axis represents binding energy usually in terms of electron-volt (eV). Along the X-axis binding energy usually plotted from higher to zero value. The binding energy of those elements is usually determined from the difference of measured kinetic energy of those ejected electrons from incident photon energy using the equation

$$E_b = h\nu - \frac{1}{2} mv^2$$

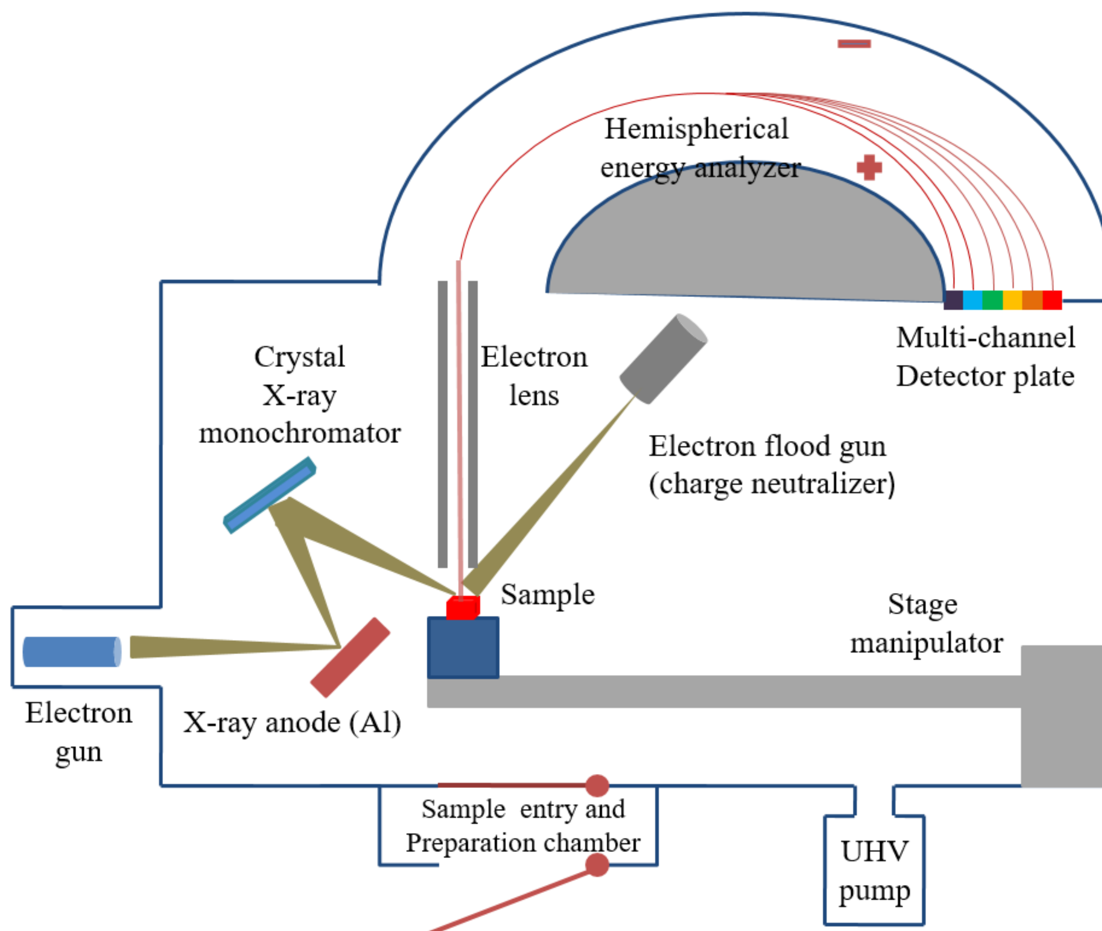

Fig. 3.11 Schematic representation of working principle of X-ray photoelectron spectroscopy

Along Y-axis the intensity which is number electron count per unit time is recorded. Typically, intensities of photoelectrons of binding energy from 1200 eV to 0 eV is measured known as survey scan. But there won't always be clearly resolved peaks for distinct elements along X-axis but have to encounter interfering peaks. In that case, curve fitting technique for overlapping peaks is utilized. From this type of fitting of photoemission peak, values of binding energy (BE), full width at half maxima (FWHM), line shape and area can also have been extracted. FWHM and line shape gives us important information about chemical environment of the atom. There may be various line shapes from narrow, symmetric to complex depending upon different oxidation states. So measuring those areas of different line-shapes, quantitative analysis of different chemical states can be analyzed.

3.1.11. Impedance analyzer

Impedance analyzer (HIOKI IM3570) is an impedance measuring instrument capable of measuring numerous electrical and electronic parameters with high speed and accuracy. It is capable of measuring electronic parameters over a long range of frequencies in the range of 4 Hz – 5 MHz with excellent speed via sweep measurement. It can simultaneously display 4 items under individual measuring conditions. This instrument can perform over a wide range of measurement conditions like different signal level and frequency range. Measurements can be performed in different modes like LCR, analyzer or continuous measurement. It is capable of measuring impedances in the range from μΩ to TΩ. Various parameters like complex impedance (Z), admittance (Y), phase shift (θ), dc resistance (R_{dc}), parallel resistance (R_p), series resistance (R_s), series capacitance (C_s), parallel capacitance (C_p), dielectric loss (D), loss tangent (δ), series inductance (L_s), parallel inductance (L_p), conductance (G), quality factor (Q) and reactance (X) can easily be measured through this device with high accuracy in a short span of time.

Fig. 3.12 Picture of impedance analyzer

Measurement of impedance characteristics over a range of frequency is known as impedance spectroscopy. Electrochemical impedance spectroscopy (EIS) is a powerful tool to analyze interfacial properties of substances. It is widely accepted in analyzing electrochemical systems and solid state devices. Complex impedance (Z) can be represented in terms of real part ($Z^{/}$) and imaginary part ($Z^{//}$) as

$$Z = Z^{/} + jZ^{//}$$

$Z^{/}$ and $Z^{//}$ physically represents resistive and reactive parts of complex impedance respectively. In order to analyze the impedance spectroscopic data, we represent Z in Argand diagram which is the basis of Nyquist plot. Basically it is the plot of imaginary part of complex impedance ($Z^{//}$) to real part of it ($Z^{/}$). An impedance measurement for a single frequency is a point on the Nyquist plot. Combination of all such points at different frequencies produces the impedance spectrum. Shapes of these plots are important in determining characteristic features. On the Nyquist plot distance any point from the origin represents modulus of complex impedance ($|Z|$) while angle made by this with X-axis represents phase angle. However Nyquist plot has a serious deficiency of not identifying frequency for a particular data point. To overcome this shortcoming, another popular presentation known as Bode plot is used. This plot is combination of frequency responses of both magnitude and phase shifts. Generally Bode plots are used in evaluating capacitive systems while Nyquist plots help in evaluating resistive systems.

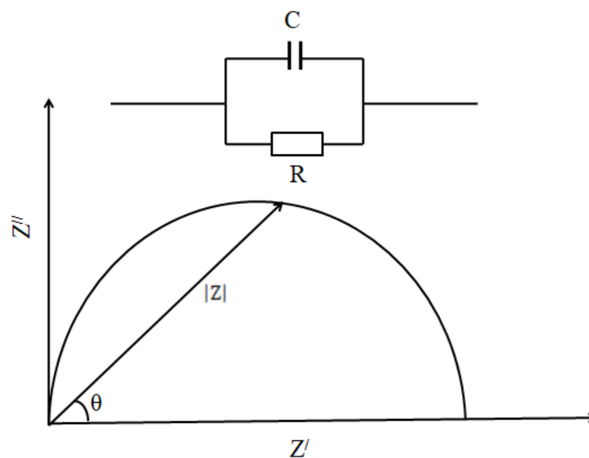

Fig. 3.13 Nyquist plot with impedance vector of a simple circuit with one time constant

These curves are very convenient in exploring charge transfer, mass transfer or diffusion process to a microscopic level. The technique to investigate these phenomenon via fitting of Nyquist plots is known as electrochemical impedance spectroscopic (EIS) analysis. Therefore, EIS technique has capability to find intrinsic information about the system about charge transfer resistance, capacitance or conductance. But in order to analyze responses, they must be compared to some equivalent model circuit. This equivalent circuit is designed to understand the individual elements constituting the complex system. But the circuit elements must be chosen according to the Nyquist plots obtained experimentally. Most of the model circuits are composed with common electric elements like resistances, capacitors and inductors. In ac impedance analysis resistance are not that important since it does not play any significant role with change in frequency and the signal remains in phase while passing through it. Applying a small ac voltage signal to the measuring unit, impedance can be determined which is contribution of charge transfer among those ions and polarization. Simply ac impedance differs to electrical resistance because a reactive component is also associated with it. In composite type of substances, there are different electric layers present which produces some kind of inhomogeneity inside it. This type of multiple electric layers induces diffusion region at those interfaces. This region is responsible for formation of double layer capacitance in the sample. Therefore, in fitting of experimentally obtained plots, a series resistance is combined with parallel combination of a resistance and capacitance as shown schematically in fig. 3.14. The parallel combination of resistance and capacitance arises due to formation of depletion layer produced at the interface of dissimilar regions. The series resistance with parallel combination is to consider the charge transfer resistance. Although in impedance measurement interfacial regions have a greater role, but similar effect arising from those core grains of a composite sample must be taken into account. So in such composites, model fitting circuit for Nyquist plots consists of a pair of such parallel combinations in series along with some series resistance. Each of these R-C combinations is a characteristic feature of a particular segment of the composite. Each R-C combination represents a particular relaxation time of that component defined as multiplication of resistance and capacitance. Thus using fitted parameters of the model circuit, relaxation times can be estimated easily. So the entire circuit may be disintegrated by distribution of some relaxation processes. In this way, impedance spectroscopic data can be transformed from frequency domain to time constant domain. In this way, microstructural information about any system can be gathered using relaxation time distribution. Relaxation time

usually means by the time required by any system to return back to its initial condition after being perturbed. We assume that the dipoles constituting any material undergo damped unforced oscillation when some external perturbation occurs. The simplest law any perturbed system follows to return back to initial condition is simple exponential decay law as follows $e^{\frac{-t}{\tau}}$. Here τ is denoted as relaxation time of the process. According to Debye relaxation process all dipoles constituting the system follows a single relaxation time. This type of relaxation occurs in those crystals which are almost perfect with very few point defects. But in reality, all practical materials involve multiple relaxation processes with broad distribution of them rather than one single relaxation time. Such system is modeled with series combination of parallel R-C circuits where each R-C represents a single relaxation behavior. Each of these relaxations emerges form a particular segment of the solid. Usually in polycrystalline material atoms are oriented in a preferred direction in a small section of the material. This section is termed as grain. But grains are oriented in random fashion constituting the whole crystal. This discontinuity in between two grains is called grain boundaries. These different segments inside the material correspond to different polarization phenomena exhibiting their existence at different frequency ranges. These type of resonant process occurs when an ac field of suitable frequency displaces those dipole constituting charge density from their equilibrium position. Different polarizations associated with this process are electronic, atomic, dipolar and space charge polarization. Electronic polarization is effective at very high frequency as high as ~ 10^{15} Hz when negatively charged electron cloud gets distorted around positively charged nucleus due to electric field. So its effect is observable only at optical frequencies. Atomic polarization is a result of dipole moment generated due to dissimilar atoms in a molecule and responding at a frequency of ~ 10^{13} Hz. Therefore, they are respondent to infrared frequency which is a characteristic of ionic solids. Orientational or dipolar polarization is a feature of polar dielectric materials with partial ionic bond. This type of polarization is observed in materials possess permanent dipole moment. When external electric field is applied dipoles try to orient themselves along the direction of applied field gives rise to this type of polarization. They show their characteristic feature in the radio frequency range of 10^6 - 10^9 Hz. Finally space charge polarization often termed as interfacial polarization seen in multiphase materials or materials having defects. This type of polarization is noticed due to accumulation of charges at vacancies which induces opposite charges at a small distance apart. This type of polarization is effective at the audio frequency range of $< 10^3$ Hz. As a whole, it is known as dielectric relaxation phenomena

involves movement of charges and dipoles due to application of ac fields. But in a dielectric polycrystalline solid, its core grains are composed of many dipoles involved in dipolar or orientational polarization. At those boundaries separating core grains, space charge region is formed which is responsible for interfacial polarization. Therefore interpreting dielectric results obtained from impedance spectroscopy, significant information about different segments of the material can be earned. Development of nanocomposite materials where of modification of boundary is involved effects the relaxation time of those boundaries while the core grains remain unchanged. Therefore, observing the relaxation time distribution of materials, any significant modification inside it can be discovered with the help of impedance spectroscopic analysis. Dielectric studies can also provide information about presence of nanofillers and host - nanofiller interaction. As relaxation time is simply proportional to dielectric permittivity, any variation in relaxation time will imply also change in dielectric characteristic. Therefore observing the variation of relaxation time distribution after nanofiller inclusion into the host, modification of dielectric characteristics can be confirmed. So impedance spectroscopy is a very convenient tool to gain a proper insight of material characteristics and their modification.

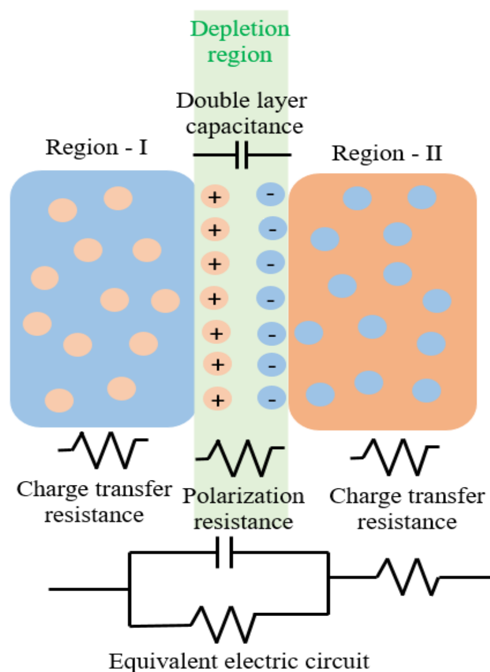

Fig. 3.14 Equivalent model electric circuit for impedance spectroscopic analysis

3.1.12. Solar simulator

Solar simulator is a device which provides illumination approximately close to natural sunlight. It is a crucial apparatus in providing solar illumination for numerous tests in laboratory environment. It is used in testing of materials or synthesis procedures related to photovoltaics, solar cell, photoluminescence, photosynthesis, aerospace materials, photo-degradation and photocatalysis. Since its intensity spectrum closely resembles to that of sun and initially it was intended to test silicon based photovoltaics, emitted wavelength lies in the region of 400 – 1100 nm. In our experiment, we have used solar simulator from photo emission technology of model #SS50AAA. This type of instrument is efficient in delivering highly accurate and collimated beam. It consist of xenon arc lamp, ellipsoidal reflector, coated mirrors, filters, beam uniformity integrating lens, collimating lens and working surface. It has several features like stable emitted light intensity, automatic stutter control, lamp life display, forced air cooling, lamp and shutter status indicator, safety interlock, forced air cooling etc. Lamp power of such solar simulator is 150 W along with lamp life time of 1500 hour.

While measuring photo responsive characteristics of prepared samples, they have been placed on the flat working surface for various measurements. The intensity of illumination can be varied by moving position of the working stage accordingly. Using this solar simulator along with source meter various important features like open circuit voltage, short circuit current, series and shunt resistance, efficiency, fill factor, rise and fall time of fabricated devices can be estimated under solar spectrum illuminated condition.

Based on the performance solar simulators can classified into several categories such as A+, A, B and C. Performances of solar simulator depends on factors like spectral match, spatial non-uniformity of irradiation and temporal instability of irradiance.

Spatial non uniformity of irradiance over an area is defined as

$$\text{Non uniformity (\%)} = \frac{\text{max irradiance} - \text{min irradiance}}{\text{max irradiance} + \text{min irradiance}} \times 100\ \%$$

To measure irradiance any photo detector can be used at different locations on the irradiation surface.

Spectral match of solar simulator is defined as its deviation in spectral irradiance from the reference spectral irradiance. It is therefore distribution of irradiation across six defined wavelength ranges.

Temporal non uniformity of a solar simulator is also related in a similar way as spatial non uniformity as

$$\text{Non uniformity } (\%) = \frac{\text{max irradiance} - \text{min irradiance}}{\text{max irradiance} + \text{min irradiance}} \times 100\ \%$$

It is a measure of stable irradiation of the solar simulator over a period of time.

The solar simulator possessing all three A category performance is designated as AAA category solar simulator.

Fig. 3.15 Picture of solar simulator

3.2. Synthesis procedure of PVDF composites

3.2.1. Materials used

Table – 3.1 Materials used and their purity

Materials	Purity
Poly (vinylidene fluoride) (PVDF)	Sigma-Aldrich (purity > 99%)
N-N-Dimethylformamide (DMF)	Sigma Aldrich (Purity>99.5%)
Acetone	Merck (Purity>98%)
Zinc acetate dihydrate	Merck (purity > 98%)
2-Propanol	Merck (purity > 99%)
Diethanolamine (DEA)	Sigma-Aldrich (purity>98%)
GO powder	Sigma-Aldrich (Purity>99%)

3.2.2. PVDF composite film deposition

3.2.2.1. Substrate cleaning

Before synthesizing nanomaterials in thin film form, substrates on which films are deposited must be cleaned properly in order to achieve optimum performance of the deposited substance. Pre-cleaning method removes water molecules, hydrocarbons and other contaminants from the substrate surface. It improves optical, electrical and other characteristics of those deposited films. Depending upon the necessity, films are deposited on different substrates like glass, fluorine doped tin oxide (FTO) coated glass or polyethylene terephthalate (PET) substrate. Primarily, these substrates are cleaned by soap solution to remove dirt

particles from its surface. Then it is washed with distilled water to clear the soap solution from it. Then it is placed inside a beaker filled with isopropanol and utlrasonacated for 10 minutes in the ultrasonicator bath. Afterwards, they are placed in a hot air oven to dry and are now ready for film deposition.

3.2.2.2. PVDF solution preparation

To synthesize PVDF thin film in membrane form, the method by Benz et al. is adopted [166]. 0.64 gm of PVDF powder is dissolved into 1:1 mixture (2 ml: 2ml) of DMF and acetone in a conical flux. This mixture is then stirred continuously for 1 hour at a temperature of 60^0 C on a hot plate magnetic stirrer until a clear transparent solution is obtained. This solution is then allowed to cool down to room temperature and is now ready for drop casting on cleaned substrates for their preparation in thin film form.

3.2.2.3. ZnO solution preparation

0.5 M (2.74 gm) zinc acetate dihydrate is dissolved into 25 ml isopropanol. This mixture is then stirred on a hot plate magnetic stirrer for 1 hour at a temperature of 60^0 C. After this the solution is stirred at room temperature for 1 more day to dissolve it better. Then, this solution is kept intact for few hours to get it in precipitate form. This precipitated compound is then dried in a hot air oven for few minutes to get it in dry powder form. This compound powder is then annealed inside the furnace for 1 hour at 450 ^{0}C to remove unwanted compounds and get pure ZnO in powder form. This prepared ZnO powder is used to prepare ZnO solution. 2 mg of this prepared ZnO power is dissolved into 50 ml isopropanol and ultrasonicated by an ultrasonicator (UR Biocoction ultrasonic cleaner) for 6 hours. In this process, finally we obtain little whitish transparent ZnO solution.

3.2.2.4. GO solution preparation

To prepare GO solution, 2 mg GO powder is mixed to 50 ml isopropanol and ultrasonicated for 6 hours for well dispersion in ultrasonic bath. This obtained black solution is then filtered by filter paper and obtained GO solution in pure and transparent form.

3.2.2.5. PVDF film deposition

To prepare PVDF in thin film form obtained PVDF solution is spin coated on fluorine doped tin oxide (FTO) or flexible polyethylene terephthalate (PET) substrates depending upon their purpose of fabrication. This solution is spin coated by a programmable spin coater (Apex Instrument) at 3000 rpm speed for 1 minute. This obtained film is then dried in a hot air oven for few minutes to remove unwanted compounds and get PVDF film in flexible, free standing, membrane form.

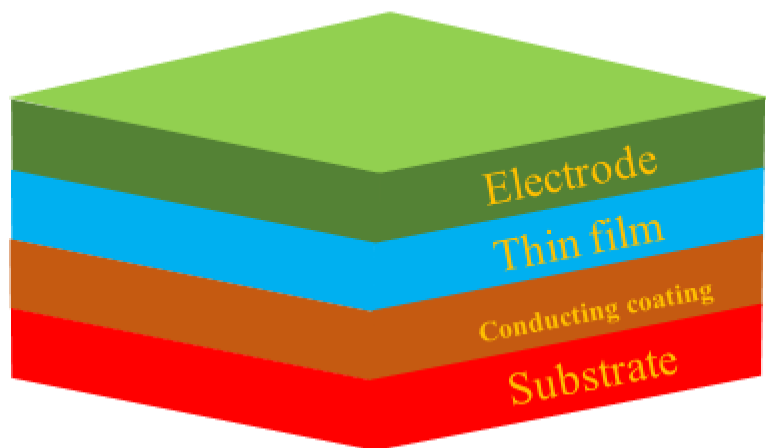

Fig. 3.16 Schematic representation of thin film

3.2.2.6. PVDF composite film deposition

To synthesize PVDF composites separately produced ZnO and/or GO solutions are added to PVDF mixture in 10% (v/v) ratio prepared by similar way mentioned earlier. Now this mixture containing ZnO and/or GO is spin coated and dried by exact similar process. In this way, PVDF composite films are synthesized. The schematic diagram of this entire process is presented in fig. 3.17.

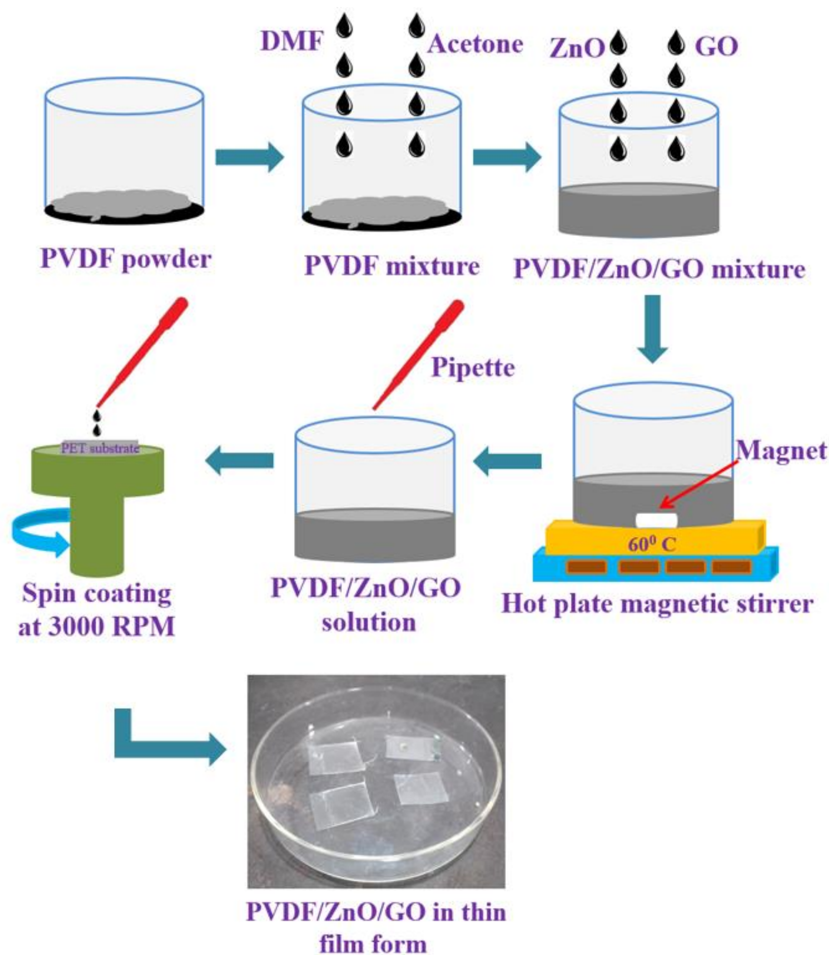

Fig. 3.17 Schematic diagram presenting synthesis procedure of PVDF composite film

3.2.2.7. PVDF/GO film deposition with variable GO concentration

To synthesize PVDF/GO composite films with variable GO concentration, PVDF solution is prepared in previous manner. Then GO solution with different amount (5, 10, 15 and 20% v/v) is mixed with previously prepared PVDF solution. This mixture is then rigorously stirred in similar way mentioned earlier. This PVDF/GO mixture is then spin coated on flexible PET substrate for 1 minute at an angular speed of 3000 rpm. This deposited film is then dried for few minutes in hot air oven at a temperature of 120° C for 10 minutes to remove unwanted compounds from those films. After drying, films are now ready for characterizations and measurements.