

2.1 Introduction of thin films

The thin film is an art of science which play a dominant role in all persistent fields of science and technology. The term thin film is used for coatings that are used to modify and increase the functionality of a bulk surface or substrate. They are used to protect surfaces from wear, improve lubricity, corrosion and chemical resistance. In many cases thin films do not change the properties of the bulk material. However, they can totally change the optical, electrical transport and thermal properties of a surface or substrate, in addition to providing an enhanced degree of surface protection. The development of novel materials is the future prospect of thin film technology. The various structures such as superlattices, nanolaminates, nanotubes, nanocomposites, smart materials, photonic band gap materials, molecularly doped polymers and structured materials have the capacity to increase the functionality of thin films. New advanced and hybrid deposition processes are being used and developed to deposit novel thin film materials and structures, which is not possible with conventional techniques [1].

A thin film is nothing but a low dimensional material created by condensing, one by one, molecular/atomic/ionic species of matter. A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. Thin films are different from thick films. A thick film is defined as a low dimensional material created by a three dimensional material or assembling large grains/aggregates/clusters of atomic/molecular/ionic species. Thin films are deposited on a substrate by various techniques [2, 3]. Thin film exhibits the following important features,

- ✓ The origin of thin films of any materials created by various deposition techniques, which starts with a random nucleation process, followed by the nucleation and growth stages.
- ✓ During thin film formation, nucleation and growth processes are mainly dependent upon various deposition parameters, such as growth temperature, growth rate and substrate chemistry, etc.
- ✓ The nucleation process can be modified significantly by external activities, such as an electron or ion bombardment.

- ✓ During the nucleation process, deposition parameter affects on film microstructure, associated defect structure and film stress.
- ✓ The crystal phase and orientation of the thin films are governed by the deposition conditions.

The basic properties of thin film, such as composition, crystal phase, orientation, thickness and microstructure are controlled by the deposition conditions [4, 5]. Thin films exhibit unique properties, which are resulting from the atomic growth process. Size effects, including quantum size effects, characterized by the thickness, crystalline orientation and multilayer aspects. The technology of thin films covers a broad spectrum spanning the thickness from a few nanometers to one micron. One considers thin films to act as the bridge between monolayer and bulk structure. The forces acting upon the atoms at the surface are different from those of the bulk.

Why thin films are important? One of the simplest reasons is that to produce desired materials with unique properties. The morphological and topographical properties of thin film of a given material depend on the kinetics of growth. Thin films have been extensively studied in relation to their applications for making electronic devices. Thin film devices for practical use were limited to passive devices such as thin film resistors and capacitors [6]. Polycrystalline thin films are typically not much dense as compared to the bulk material of the same composition. They are frequently under a state of stress depending on the conditions of deposition. The microstructure of thin films can be quite different than the bulk material with respect to grain size and texture. Kinetic effects are considerably different in thin films than in bulk. Thin film processes are essential to make nanometer materials, such as quantum dots, quantum wires and superlattices. The consequence of all these makes thin film studies not only more interesting, but also provides considerable challenges in gaining the physical understanding of phenomena. Thin film behavior is closely associated with the presence of surface when two solids are in intimate contact with each other, where the properties differ from those of the bulk properties, which it separates.

As a two dimensional system thin films are of great importance to many real world problems. The cost of thin film materials is less as compared to the corresponding bulk material when it comes to surface processes. In order to develop

new technologies for future application, it is important to utilize knowledge and determination of the nature, functions and new properties of thin films. Some of the important applications of thin films are in technology of industries, including microelectronics, optoelectronics, communication, sensors, catalysis, coating (for examples mirror in lasers and in telescopes) as well as in energy generation and conservation strategies. Therefore, the impact of thin film science and technology in our modern life is enormous. In the other word, thin films are currently used in various aspects of both daily life and sophisticated as well as hi-tech applications [7].

2.2 Thin film synthesis techniques

An emerging technology needs thin films of new materials for a different promising application. The thin film can be a single/multi component, multilayer coating on substrates of different shapes and sizes. The thin film properties are required for a particular application can be brought about by using various synthesis techniques [8-10].

The optical absorption, crystal structure, morphology, composition and electrical properties of thin films are extremely sensitive to the synthesis techniques and preparative parameters. Several methods have been employed for the synthesis of metals, alloys, ceramic, polymer, semiconductors and superconductors on different substrate materials. Each method has its advantages and disadvantages. No one technique is ideal to deposit the thin films covering all the desired aspects such as cost of equipments, deposition parameters and nature of the substrate material. The performance and fabrication cost of thin film material depend on synthesis methods, which are used to produce devices. The vast varieties of thin film synthesis techniques are used to fabricate thin film devices. It is possible to classify these techniques in two ways [11, 12].

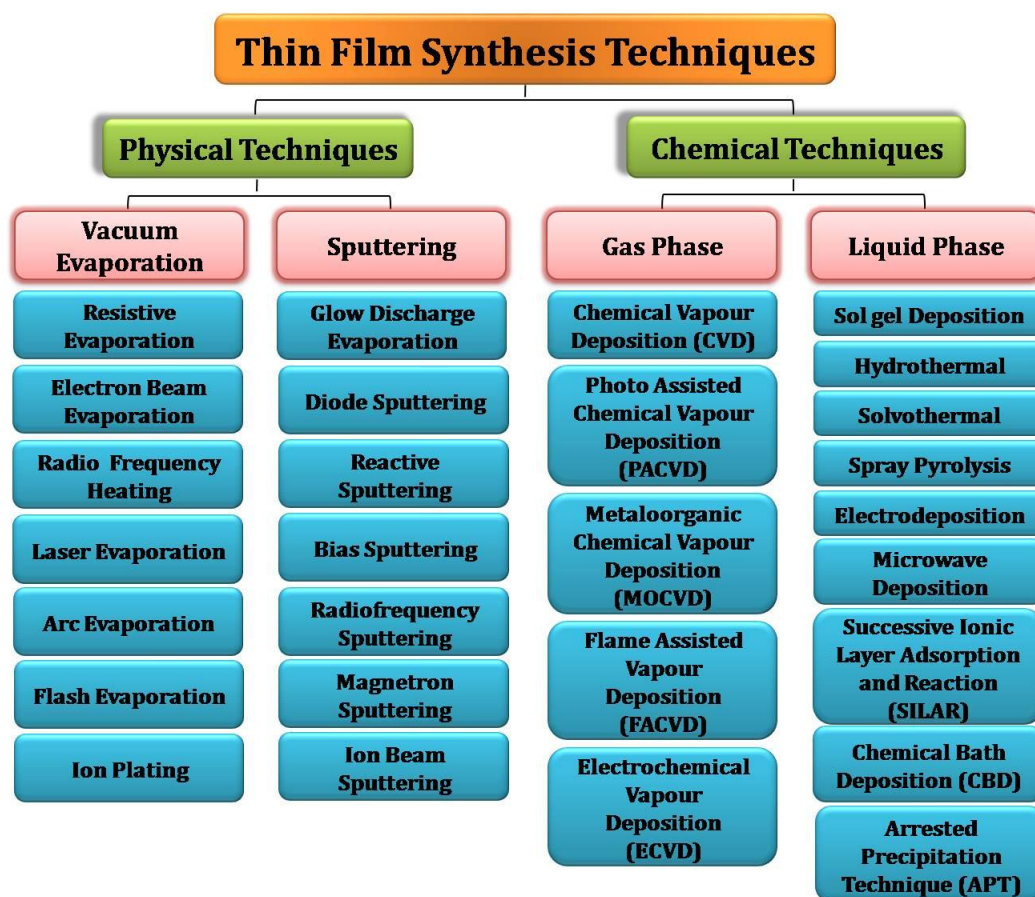
Physical Technique

Chemical Technique

Physical method deals with the evaporation or ejection of the material from a source, i.e. evaporation or sputtering, whereas chemical methods depend on physical properties. Structure-property relationships are the key features of such devices and basis of thin film technologies. The chemical technique is that provides a growing thin films of metal alloys, compound semiconductors and amorphous or crystalline

compounds of different stoichiometry. The basic principle of this method is a chemical reaction between volatile/non-volatile compound of the material from which the film is to be synthesized on the substrate support. The chemical reaction depends on specific conditions like pH, deposition time, bath temperature, precursor concentration, etc [13]. A brief introduction of thin film synthesis techniques is presented in Table. 2.1.

Table. 2.1 A brief introduction of thin film synthesis techniques.



2.2.1 Physical Techniques

Basically, thin film synthesis by the physical techniques is based on the formation of vapour of the material to be coated as a thin film. The material in solid form is either heated until evaporation (vacuum evaporation) or sputtered by ions (sputtering) [14, 15]. The merits of physical techniques are laid in dry processing, high purity and cleanliness, compatible with semiconductor integrated circuit processing and epitaxial film growth. However, there are certain disadvantages such as slow deposition rates, difficult to control stoichiometry, high temperature, post

annealing treatment often required for crystallization and high capital expenditure [16].

The physical techniques are further divided into two categories,

A) Vacuum Evaporation

B) Sputtering

A) Vacuum evaporation

Although evaporation is the one of the oldest techniques used for depositing thin films, i.e. thermal evaporation or vacuum evaporation. These techniques are still widely used in the laboratory and in industry scale for depositing metal and metal alloys [16]. The following sequential basic steps involved in vacuum evaporation,

- (i) The vapour is generated by boiling or subliming a source material,
- (ii) The vapor is transported from the source to the substrate and
- (iii) The vapor is condensed to a solid film on the substrate surface.

The vacuum evaporation technique is divided into different techniques, which are as follows,

❖ **Resistive evaporation**

The metal, alloys and many other new materials are synthesized by using this technique. It is very simple and convenient technique of evaporation. It requires only sufficient vacuum environment. Sufficient amount of heat is given to the substance to attain the necessary vapour pressure for the evaporation in this method. The evaporated materials/compounds deposited on a substrate kept at a suitable temperature. The oldest process is evaporation from a boat or a wire, which consists of a refractory metal (W, Ta, or Mo), heated by an electric current. Vapor sources of different designs are used for evaporation depending on the evaporant material [17, 18].

❖ **Electron beam evaporation**

In this technique a beam of electron is accelerated through a field of 5 KeV to 10 keV and is focused onto the surface of the material for evaporation. The electrons bombard rapidly on the surface and material melts at the surface and evaporates. This allows synthesis of high purity thin films because crucible materials or their

reaction products are practically excluded from evaporation [5]. The electrons emitted from a tungsten cathode are accelerated by high voltages and are focused on the substance to be evaporated, which is put in a water-cooled crucible. The kinetic energy of the electrons is transformed into thermal energy, so that the material in the crucible melts and evaporates into the vacuum.

❖ **Radio frequency heating**

Radio frequency can be used to heat the evaporant by a suitable arrangement of RF coils, levitation and evaporation can be achieved, thereby eliminating the possibility of contamination of the film by the support crucible. The radio frequency heating, includes the heating materials by the application of radiowaves having high frequency (above 70,000 hertz, (cycles per second)). This method is again divided into two sub methods. One of these, induction heating is highly effective for heating metals and other materials that are relatively good electrical conductors. The other method, called dielectric heating, is used with materials that are poor conductors of electricity.

❖ **Laser evaporation**

For the ejection of particles into vacuum the high power, pulsed laser beams can be used. The laser source, kept outside the vacuum system, is focused onto the target material, and the ejected material is deposited on the substrate, placed in front of the target material in the vacuum system. An advantage of laser evaporation is that its high energy, alloys can be deposited without a change of composition as in flash evaporation techniques.

❖ **Arc evaporation**

The arc evaporation method is used to apply aluminum, titanium, zirconium and chromium based hard material coatings for tools. The starting material for this vacuum based coating process takes the form of an arc cathode. In this process, an arc with a diameter of just a few microns is run over the solid, metallic coating material, causing it to evaporate. Because of the high currents and power densities used, the evaporated material is almost totally ionized and forms a high energy plasma. Theoretically the arc is a self sustaining discharge capable of sustaining large

currents through electron emission from the cathode surface and the rebombardment of the surface of positive ions under high vacuum conditions.

❖ Flash evaporation

Flash evaporation is one of the important technique for the synthesis of thin films alloys whose constituents have different vapor pressures. This technique requires only one boat maintained at sufficiently high temperature to evaporate the less volatile component of the alloy. This technique does not require maintaining the critical vapor pressures of the components and temperature of the boat unlike multisource thermal evaporation, which is a main advantage of this technique. In flash evaporation, the selected alloy is prepared in powder form with grain size as small as possible and is dropped onto a boat that is hot enough to make sure that the material is evaporated instantly.

The most common problem encountered in the flash filament is incomplete evaporation of powder from flat filament due to particle deflection and rejection. The sudden release of gases from the filament is often sufficient to expel particles. Another loss mechanism is the deflection of falling powder from the filament due to rising vapour. The small particles are deflected more easily than larger ones may due to use of graded powders. The evaporation of pure powders such as compound or alloys, particle ejection and deflection has an effect on the economy of the process and maintenance of the vacuum system. There is also risk that particles may throw against the substrate surface. To avoid these difficulties, coarse powder or cylindrical or conical crucible has been used in the evaporation of precursors.

❖ Ion plating

The main characteristic of the ion plating technique is to use the bombardment of ions to interfere in the plating process. By making use of the activity of plasma and the bombardment effect, the energy exchange between ions, their substrate interfaces. The growing thin film compounds can be brought into existence under a temperature much lower than that conditioned by traditional thermodynamics. While, the properties such as, density of the films, adhesion between film/substrates and structure of the films are improved. Ion plating technique combined the technique of glow discharge or arc discharge of a gas,

plasma technique and vacuum evaporation plating technique. In this process source is a thermal evaporation in ordinary evaporation techniques, and a glow discharge is maintained at a pressure of 10^{-1} torr to 10^{-2} torr. Particularly, the source crucible or filament acts as the anode and the substrate as the cathode.

B) Sputtering

The sputtering is the most versatile technique tremendously used for the synthesis of thin films. Using this technique desired composition in films with good adherence will be maintained. Whereas, it permits the better control of film thickness. The sputtering process involves the formation of gas plasma usually an inert gas such as argon by applying voltage between cathode and anode electrodes [19]. Generally, in sputtering the ejection of surface atoms from an electrode surface by momentum transfer from bombarding ions to surface atoms. From this definition, sputtering is clearly an etching process, and used for surface cleaning and pattern delineation. The sputtering process produces a vapour of material electrode. This technique frequently used as method of thin film deposition like evaporation method. Therefore, sputter deposition is a generic name for a variety of processes [2].

❖ Glow discharge sputtering

The glow discharge sputtering is an very simplest arrangement of sputtering technique. In an inert gas at low pressure electric field is applied between two electrodes. The cathode is a material to be deposited and a substrate is coated on the anode as a target. When the electric field is applied glow discharge is produced and the positive gas ion impact on the target plate and cathode material atoms will be ejected. These ejected atoms eventually condense on the substrate as a thin film coating. The electrode and gas phase phenomena in various kinds of glow discharges (especially RF discharges) represent a rich source of the route used to deposit and etching of thin films. Creative exploitation of these phenomena has resulted in the development of many useful processes for film deposition as well as etching process [2].

❖ Diode sputtering

Diode sputtering uses a plate of the material to be deposited as the cathode (or RF Powered) electrode (target) in a glow discharge. Thus, material can be transported from the target to a substrate to form a thin film. Films of pure metals or alloys can be deposited when using noble gas discharges (typically Ar) with metal targets.

❖ Reactive sputtering

Compounds can be synthesized by reactive sputtering, that is sputtering elemental or alloy targets in reactive gases. Alternatively, they can be deposited directly from compound targets.

❖ Bias sputtering

In this case the substrates are biased with a negative potential with respect to an anode so that it is subjected to an ion bombardment throughout the growth. This effectively cleans the substrate surface, and films with good adhesion to the substrates are formed. During the film synthesis ion bombardment can produce one or more desirable effects, such as resputtering of loosely bonded film material, low energy ion implantation, desorption of gases, conformal coverage of the surface, or modification of a large number of film properties.

❖ RF sputtering

This can be used to sputter insulator films directly and also possible to sputter at low pressures. In this case an RF potential is applied to the metal electrode placed behind the dielectric plate target. In DC systems, positive charge builds up on the cathode (target) need 1012 volts to sputter insulators. Also, avoid charges build up by alternating potential. The sputter deposition occurs when the target is negative and the substrate and chamber make a very large electrode, so not much sputtering of substrate.

❖ Magnetron sputtering

Another alternative in sputtering sources that uses magnetic field transverse to the electric fields at sputtering/target surfaces, which is known as magnetron

sputtering. Sputtering with a transverse magnetic field produces several important modifications of the basic processes. Target generated secondary electrons do not bombard substrates because they are trapped in cycloidal trajectories near the target, and thus do not contribute to increased substrate temperature and radiation damage [20]. In magnetron sputtering sources produces higher deposition rates than conventional sources, beneficial for economic, large area industrial application. There are cylindrical, conical, and planar magnetron sources, all with particular advantages and disadvantages for specific applications. As with other forms of sputtering, magnetron sources can be used in a reactive sputtering mode.

❖ Ion beam sputtering

Ion beams, produced and extracted from glow discharges in a differently pumped system, are important to scientific investigations of sputtering, and are proving to be useful as practical thin film deposition systems for special materials in a relatively small substrate area. There are several advantages of ion beam sputtering deposition. The target and substrate are situated in a high vacuum environment rather than in a high pressure glow discharge. Glow discharge artifacts are thereby avoided, and usually results in the formation of high purity films [21].

2.2.2 Chemical techniques

The chemical synthesis refers to the synthesis of thin film on a solid substrate from a reaction occurring in a solution (almost in aqueous medium). The chemical techniques are based on either slow release of ions or slow decomposition of a complex compound. However, lots of techniques are not involved these slow steps that sometimes called chemical deposition. The chemical methods are the most important for the growth and fabrication of the thin films owing to their versatility for synthesis of new compounds at relatively low temperature. Highly crystalline layers, with a high purity thin films can be deposited with required stoichiometry. The processes are economical and have been industrially exploited to large scale. The chemical techniques are divided into two categories,

A) Gas phase

B) Liquid phase

A) Gas phase

Generally, in gas phase methods of thin film formation by the pure chemical processes in the gas or vapor phases. The deposition technology has turned into one of the most important means for producing thin films and coatings of a very large diversity of materials necessary for advanced technology. Particularly in solid state electronics where the most requirements such as, refined purity and composition must be controlled. In fact, if the gas flow continues for too long (typically more than a few minutes), the film tends to break up and precipitate. Since the substrate for these films is a liquid surface and the films can be picked up and transferred to another surface or possibly even be self supporting in small areas.

❖ Chemical vapour deposition

Chemical vapor deposition (CVD) is a chemical technique for the synthesis of thin film of different materials. In a typical CVD process the substrate is exposed to one or more volatile precursors, which react or decompose on the substrate surface to synthesize the desired material. Frequently, volatile byproducts are also produced, which are removed by gas flow through the reaction chamber. CVD [22-25] is a synthesis process in which constituents of the vapor phase react chemically near or on a substrate surface to form a solid product. The deposition technology has become one of the most important means for creating thin films and coatings of a very large variety of the purity and composition. CVD is tremendously used in the semiconductor industry, for the semiconductor device fabrication process, includes, polycrystalline, amorphous and epitaxial silicon, SiO₂, silicon germanium, tungsten, silicon nitride, silicon oxynitride and titanium nitride. Also, the CVD process is used for the production synthetic diamonds.

CVD offers many advantages over other deposition processes. These include,

- ✓ Versatile - can deposit any element or compound.
- ✓ High Purity - typically 99.99 %.
- ✓ High Density - nearly 100 % of theoretical.
- ✓ Material formation well below the melting point.
- ✓ Coatings deposited by CVD are conformal and near net shape.
- ✓ Economical in production, since many parts can be coated at the same time.

❖ Photo assisted chemical vapour deposition

PACVD technique is based on activation of the reactants in the gas or vapor phase by electromagnetic radiation. Selective absorption of photon energy by the reactant molecules or atoms initiates the process by forming reactive free radical species that interact to form a desired film product. Mercury vapor is usually added to the reactant gas mixture as a photosensitizer that can be activated with the radiation from a high intensity quartz mercury resonance lamp (253.7 nm wavelength).

❖ Metalorganic chemical vapour deposition

The heating of organometallic solution that evaporate and deposited on the heated substrate surface, therefore it is called as, metal organic chemical vapor deposition (MOCVD) technique. It is the chemical vapour deposition method of epitaxial growth of materials, especially compound semiconductors from the surface reaction of organic compounds or metal organics and metal hydrides containing the required chemical elements. The films grown by this method, generally requires expensive, sophisticated apparatus. MOCVD possesses the potential for large area deposition, composition control, film uniformity and high film deposition rates [26]. MOCVD has a great deal of technological importance in the fabrication of a number of optoelectronic and high speed electronic devices.

❖ Flame assisted chemical vapour deposition

Flame assisted chemical vapour deposition (FACVD) is a low cost and simple atmospheric pressure CVD technique that is compatible with both small volume and high volume continuous coating processes. Use of this method with less hazardous aqueous solution of simple metal salts can yield metal oxide thin films. Therefore, this method has a major advantage in terms of cost of precursor and environmental impact compared to CVD methods. In FACVD, the flame is used to supply the required energy to crack the precursor species into fragments which subsequently form the thin film on the substrate surface. The main advantage of this technique is that closed reaction cell is not essential, so making it ideal for fitting on open production lines. However, as an open air process, the atmospheric impurities may be contaminated

during FACVD process, which can lead to contamination within the desired thin film material.

❖ Electrochemical vapour deposition

Electrochemical vapour deposition is one of the oldest and most widely used techniques for fabrication of thin films. In deposition reaction potential is more intensive and energy efficient than thermal processes, resulting in more economic production of good quality material. Contrary to the vacuum based technologies such as physical vapor deposition and chemical vapor deposition, electrochemical vapour deposition is carried out in the liquid electrolyte containing ions, which can be incorporated in the deposit, during deposition and become an impurity of the deposited thin film. The electrolyte is a major impurity source, and it is practically impossible to remove the impurity completely [27].

B) Liquid phase

The liquid phase deposition techniques are the most important tools for the deposition of the different types of compound thin films at an ambient temperature. The growth of inorganic thin films from liquid phases by chemical reactions is fulfilled by chemical synthesis techniques.

❖ Sol gel synthesis

Sol gel has emerged in the last 20th century as a versatile, alternative method to produce ceramic materials, organic-inorganic hybrid without going to drastic thermal treatment. The sol gel process involves the transition of a solution system from a liquid "sol" (mostly colloidal) into a solid "gel" phase. Through the sol gel process, it is possible to fabricate different materials in a wide variety of forms such as, ultrafine or spherical shaped powders, thin film, fibers, porous or dense materials and extremely porous aerogel materials. This technique covers large market and touches many industrial and technological domains from applied biomedical to physics. In addition, it is particularly well adapted to thin film fabrication as a results possibility to tune and control the desired properties. In this technique precursor and other solutes can be of different nature and dissolved/suspended in the liquid. The sol gel coating process takes place as follows,

- ✓ The desired colloidal particles once dispersed in a liquid to form a sol.
- ✓ The deposition of sol solution on the substrate surface is carried out by using spraying, dipping or spinning.
- ✓ The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.
- ✓ To form amorphous crystalline coating final heat treatment is given to pyrolyse the remaining organic and inorganic components.

❖ Hydrothermal synthesis

The Hydrothermal synthesis technique has been the most popular technique and increased interest from scientists and technologists of different disciplines. The word “hydrothermal” has geological origin. A self explanatory word, “hydro” meaning water and “thermal” meaning heat. British Geologist, Sir Roderick Murchison (1792–1871) was used this word for the first time, to describe the action of water [28]. Hydrothermal processing can be defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions. Hydrothermal method is used to synthesize different chemical compounds and materials using a closed system. The physical and chemical processes flowing in aqueous solutions at temperature above 100°C and pressures above 1 atm. The reaction kinetics and properties of the resulting products totally depends upon the initial pH of the solution, duration, temperature of synthesis and pressure in the system [29, 30]. The synthesis is carried out in sealed autoclaves which are closed in steel cylinders that can withstand at high temperatures and pressure for a long time. Advantages of the hydrothermal synthesis technique include the ability to control, purity, composition, size and shape of crystals [31].

The hydrothermal synthesis of materials is nothing but solution processing and it can be described as super heated aqueous solution processing. Besides, for processing nanomaterials, the hydrothermal technique offers special advantages because of the highly controlled diffusivity in a strong solvent medium in a closed system. Nanomaterials require control over their physico-chemical characteristics. As the size is reduced to the nanometer range, the materials exhibit interesting

chemical and physical properties compared to their conventional coarse grained counterparts due to a size quantization effect.

❖ Solvothermal synthesis

Solvothermal synthesis is a technique used for synthesis of a various materials i.e. polymers, ceramics, metals and semiconductors. The process involves the use of a solvent under high pressure (1 atm and 10,000 atm) and temperature (typically between 100 °C and 1000 °C) that facilitates the interaction of precursors during synthesis. When water is used as the solvent, the method is called “hydrothermal synthesis.” Usually below the supercritical temperature of water (374 °C) the hydrothermal synthesis is performed. It can be used to prepare many materials such as, thin films, single crystals, nanocrystals and bulk powder. In addition to this, by optimizing the concentration of the solution, growth kinetics and solvent supersaturation the morphology of the crystals is controlled. Over the last few decades, a majority (~80 %) of the literature indicated that, most of researchers attention has been focused on synthesis of nanocrystals through solvothermal synthesis technique.

❖ Spray pyrolysis

Numerous materials have been prepared in the form of thin films due to their potential technical value and scientific curiosity in their properties. A number of techniques have been examined in the search for the most reliable and cheapest method for the synthesis of thin films. These include oxidation of an evaporated metal in reactive and nonreactive sputtering techniques, chemical vapour deposition, etc. and a number of methods involving growth from chemical, so-called chemical techniques. Considering their simplicity and inexpensiveness, chemical techniques have been studied extensively for the synthesis of different thin film compounds. Spray pyrolysis is the simplicity of the apparatus and good productivity of large scale it offered a most attractive way for the formation of thin films of the noble metals, metal oxides, spinel oxides, chalcogenides and superconducting compounds [32]. Spray pyrolysis is the process in which a film is synthesized by spraying a solution on a heated substrate surface, in which constituent react to form chemical compounds. The selected chemical reactants are having desired product with volatile compounds

at deposition temperature. The substrate provides thermal energy for the decomposition and subsequent recombination of constituent species followed by sintering and crystallization of clusters and results in the formation of thin films. The required thermal energy is different for the different materials and the various solvents used in the spray process. The properties of the deposited thin film depend on the precursor solution composition, substrate temperature, spraying rate, carrier gas, ambient atmosphere, droplet size and cooling rate after deposition [33, 34].

❖ Electrodeposition

When the chemical changes occur due to the passage of electric current through an electrolyte is called electrolysis. Electroplating is frequently called as "electrodeposition". Deposition of any substance on an electrode as a consequence of electrolysis is called electrodeposition. As a matter of fact, "electroplating" can be considered to occur in the process of electrodeposition. It's a process using electrical current to reduce cations of a desired material from a solution and coat that material as a thin film onto a conductive substrate surface [35, 36]. Since its invention in 1805 by Italian chemist, Luigi Brugnatelli, electroplating has become an extensively used industrial coating technology. Its applications such as,

- ✓ Decoration: Coating of more expensive metal onto a base metal surface in order to improve the appearance. Applications in jewellery, furniture fittings, hardware and tableware.
- ✓ Protection: Corrosion resistant coatings such as chromium plating of automobile parts and domestic appliances. Zinc and cadmium plating of nuts, screws and electrical components. Wear resistant coatings such as nickel or chromium plating of bearing surfaces and shafts and journals.
- ✓ Electroforming: Manufacture of sieves, screens, dry shaver heads, record stampers, molds, and dies.
- ✓ Enhancement: coatings with improved electrical and thermal conductivity, solderability, reflectivity etc.

The electrode gains a certain charge on itself, which attracts oppositely charged ions and molecules holding them at the electrode electrolyte interface. During electrodeposition, ion reaches the electrode surface, stabilizes on it, releases their charges and undergoes electrochemical reaction. The rapid layer depletion of

the depositing ions from the double layer is compensated by a continuous supply of fresh ions from the bulk electrolyte. The factors affecting the electrodeposition process are current, pH of an electrolyte, bath composition, agitation, temperature of bath solution and the shape of electrode [18]. The electrodeposition process is well suited to make films of metals such as copper, gold and nickel. The films can be made in any thickness from $\sim 1\text{ }\mu\text{m}$ to $> 100\text{ }\mu\text{m}$. The deposition is best controlled when used with an external electrical potential, however, it requires electrical contact to the substrate when immersed in the liquid bath.

❖ Microwave synthesis

Microwave assisted synthesis is emerging as a new lead synthesis technique in synthetic materials chemistry. The technique offers the synthesis of different compounds in simple, clean, fast, efficient, and economic route. In the recent year microwave assisted organic reaction has emerged as a new tool in organic synthesis. An important advantage of this technology includes high acceleration rate of the reaction, decrease in reaction time with an improvement in the yield and quality of the product. This technology has the potential to have a large impact on the fields of screening, combinatorial chemistry, medicinal chemistry and drug development and therefore still used under the laboratory scale. In general, synthesis methods have tedious apparatus set up, longer heating time and excessive use of solvents/reagents which result in an increase in the overall cost of the process. In the microwave heating, use of electromagnetic waves ranges from 0.01 m to 1 m wavelength of certain frequency to generate heat in the material. These microwaves lie in the region of the electromagnetic spectrum between IR and radio wave. They are defined as those waves with wavelengths between 0.01 m to 1 m, corresponding to the frequency of 30 GHz to 0.3 GHz [37, 38].

The basic principle behind the heating in microwave oven is due to the interaction of charge atoms of the reaction material with an electromagnetic wavelength of particular frequencies. It is generally accepted that, in a liquid bath, constant reorientation created by the interaction of the dipole moment of the molecules in high frequency electromagnetic radiation leads to a friction and collisions between molecules, which subsequently generates heat [39, 40]. When applying microwave irradiation in a chemical bath, the reaction time can be reduced

quickly. Meanwhile, the adherence between films and substrates can be increased tremendously than that subject to conventional heating.

❖ Successive ionic layer adsorption and reaction

Thin films are obtained using SILAR technique by successive immersion of substrate into separately placed cationic and anionic precursors solution followed by rinsing between every immersion with ion-exchanged water/alcohol. This results in precipitation formation and wastage of the solution are avoided. The SILAR is based on sequential reaction on the substrate surface and rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution. The SILAR process is intended to grow thin films of water insoluble ionic or ion covalent compounds by heterogeneous chemical reaction at the solid solution interface between adsorbed cations and anion [41]. The SILAR results in pinhole free and uniform deposits, since the basic building blocks are ions instead of atoms.

❖ Chemical bath deposition

Lots of techniques are available in the recent times and used by researchers in the deposition of thin films of different materials on various substrates. Chemical bath deposition (CBD) has of great commercial value than other techniques and has attracted the attention of researchers today due to its simplicity, convenience, reproducibility, large area deposition and commercial production. The solution growth technique was pioneered by the works of Bode and co-workers at Santa Barbara Research Centre, Kitaev and co-workers at Ural Polytechnic (Kitaev & Terekhova, 1970). The technique itself was first used in 1946 to synthesize PbS thin films for infrared applications [42]. The main feature of CBD is that it requires a simple solution bath and substrate mounting devices. The wastage of bath solution after each deposition is the one of the disadvantages of this method. Through the relatively simple process, CBD yields well adherent and homogeneous thin films with good reproducibility. The growth of thin film strongly depends on various growth conditions, such as the temperature of the solution, duration of deposition, composition and the chemical nature of the substrate. The CBD is widely used for

synthesis of chalcogenide, oxide thin films onto different substrates such as glass, steel and conducting glass etc.

In chemical techniques two types of nucleation take place in bath solution: homogeneous and heterogeneous nucleation. The rapid formation of larger particles throughout the solution, as precipitate is nothing but homogeneous nucleation process. While, heterogeneous nucleation occurs at the substrate surface and particles grow slowly to form a thin film. The CBD involves two steps, nucleation and particle growth, and is based on the formation of solid phase from a solution [43]. The chemical synthesis can synthesize any compound that satisfies following basic necessities,

- ✓ The compound can be produced by simple precipitation.
- ✓ The compound should be chemically stable in the solution.
- ✓ If the reaction proceeds via the free anion, then this anion should be relatively slowly generated.

❖ Arrested precipitation technique

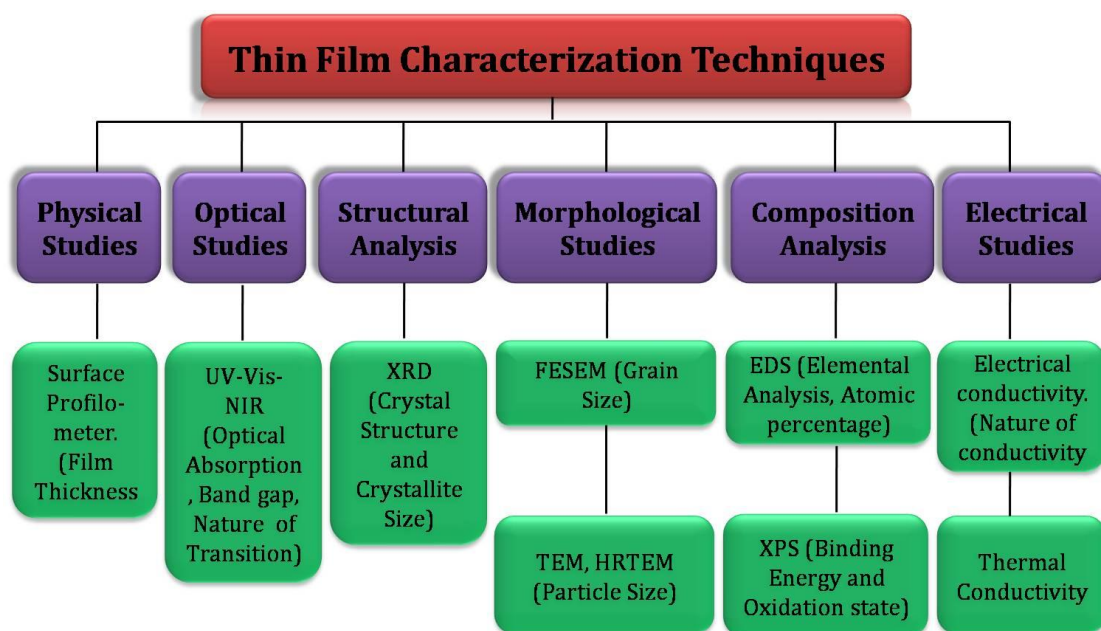
The APT is also called as controlled precipitation technique and it is a modified CBD technique, based on controlled release of metal ions and involves kinetically controlled nucleation of metal chalcogenides [44]. It is characterized by simple formulation of set up, low temperature processing and has potential to replace expensive, sophisticated technique. Also the properties of desired compound can be tuned by optimizing the pH of the bath solution, precursor concentration, deposition time, temperature. The controlled dissociation/release of metal ions facilitated through arrested metal ions by a stable complexing agent such as, triethanolamine (TEA), ethylenediaminetetraacetic acid (EDTA), tartaric acid (TA), citric acid, etc. The thin film formation involves creation of a nucleation center at the substrate surface followed by growth of metal chalcogenide by ion by ion condensation followed by multinucleation of appropriate ions from bound stable complexes. The APT is based on Ostwald ripening process. Initially, a small nucleus or embryo comes closer to each other and form a larger crystal, the ions formed by partial dissolution of the smaller, less stable crystal can be incorporated into the larger stable crystal. As the smaller crystal becomes even smaller, its dissolution will become more favorable and eventually it will disappear. The further result is that the

larger crystals grow at the expense of the smaller ones. If the concentration of particles is sufficiently increased/high, then the probability of collisions between these particles becomes more. Result in either aggregation or coalescence. When two particles approach each other, the Van der Waals force of attraction between them will often cause them to stick together. This can continue until a large particle comprising the individual particles has formed. This is the process of aggregation, and the resulting large particle is called an aggregate. The important characteristic features of APT are as follows,

- ✓ It is simple, cost effective, self organized growth process and does not require sophisticated instrumentation.
- ✓ The synthesis is carried out at low temperature and avoids oxidation or corrosion of the metallic substrates.
- ✓ Slow film formation process is favorable for improvement in surface morphology with enhanced grain structures over the substrate surface.
- ✓ It is best suited for large area depositions of thin film.
- ✓ For synthesis of doped and mixed films, mixant/dopant solution added directly into the reaction bath.
- ✓ The electrical conductivity of the substrate material is not an important criterion.
- ✓ An intimate contact between reacting species and the substrate material permit uniform and pinhole free deposition on the substrate surface.
- ✓ Dissociation of organometallic complexes to release free metal ions for reaction well controlled by maintaining the pH of reaction bath.

2.3 Thin film characterization techniques

The advancement in science has been takes place mainly with the discovery of new semiconducting thin film materials for different applications [45]. Control and knowledge of preparation conditions are not only necessary for the production of high quality thin film for specific applications, but a prerequisite characterization also important. Characterization is an important step in the advancement of unknown materials [46].

Table. 2.2 Summary of thin film characterization techniques

Each technique has a special niche which is based on the information it provides that is not available from other analytical techniques. The complete characterization of any material consists of phase analysis, surface characterization, compositional characterization and microstructural analysis, which has strong relevance with the properties of materials [47]. This has led to the emergence of a variety of advanced techniques in the field of materials science. In this section different analytical instrumental techniques used to characterize the deposited thin films are illustrated with significant principles of their operation and working mechanism. Table. 2.2 shows various characterization techniques.

➤ Technique for physical studies

2.3.1 Surface profilometer

Fig. 2.1 shows photograph of surface profilometer. Thickness measurement can be carried out by two different methods. One is weight difference density method and another is surface profilometry. The weight difference method is time consuming, so surface profilometer is superior to measure thickness of the thin film. Reproducibility in properties is achieved only when the film thickness and preparative parameters are kept constant. Actually, the surface profilometer is a

reliable method for film thickness measurement. In this method cross sectional area and weight of thin film deposited on substrate support is measured.

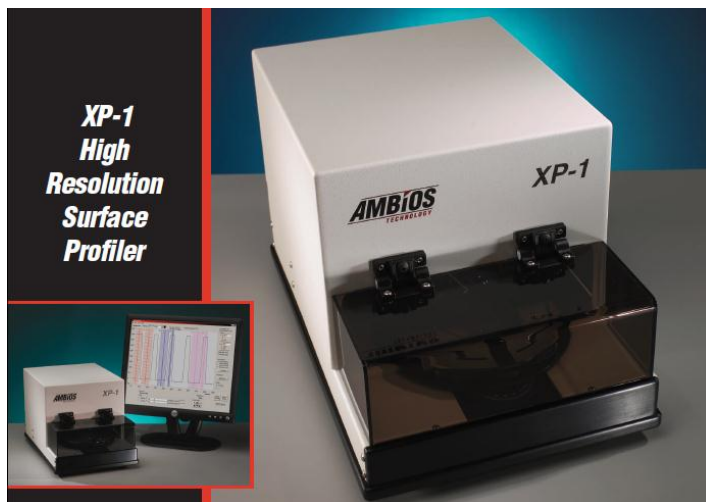


Fig. 2.1 Photograph of surface profilometer.

<http://www.ambros.ru/files/u1/XP-1brochure.pdf>

An electromagnetic sensor detects the vertical motion of the stylus as it is moved horizontally across the sample surface (thin film) under investigation. It can be used for the measurement of,

- ✓ Film thickness (Step height).
- ✓ Roughness.
- ✓ Change of 200 Å to 65 μm .
- ✓ Vertical resolution of about 10 Å. But the horizontal resolution depends upon the tip radius.

➤ Techniques for optical studies

2.3.2 UV-Vis-NIR spectrophotometer

UV-Vis-NIR spectrophotometer measures the light absorption, as a function of wavelength. The band structure in semiconductors can be determined by using the optical absorption studies (Fig. 2.2). We can determine the optical band gap of a material as well as determine whether the valence band and conduction band extrema occur at the same or different points in the k-space, knowing the frequency dependence of the absorption processes [48]. UV-Vis-NIR spectroscopy is based on the Beers-Lamberts law. The Beer-Lambert law (or Beer's law) is the linear

relationship between absorbance and concentration of an absorbing species. The general Beer-Lambert law is usually written as equation 2.1 [49]

$$A = \alpha \times b \times c \quad 2.1.$$

where 'A' is the measured absorbance, ' α ' is an absorption coefficient, 'b' is the path length, and 'c' is the analyte concentration.



Fig. 2.2 Photograph of UV-Vis-NIR spectrophotometer.

http://www.bergman.no/getfile.php/Bilder/Artikkelbilder/Shimadzu/UV1800_large.jpg

The two types of band gap semiconductor, a direct band gap and an indirect band gap. The energy band diagram of a semiconductor is complex and depends on the direction in the crystal. The energy is plotted as a function of momentum (k), along the main crystallographic directions in the crystal. The minimum energy state in the conduction band and the maximum energy state in the valence band are each characterized by a certain crystal momentum (k -vector). Fig. 2.3 shows a schematic ray diagram of direct and indirect transition.

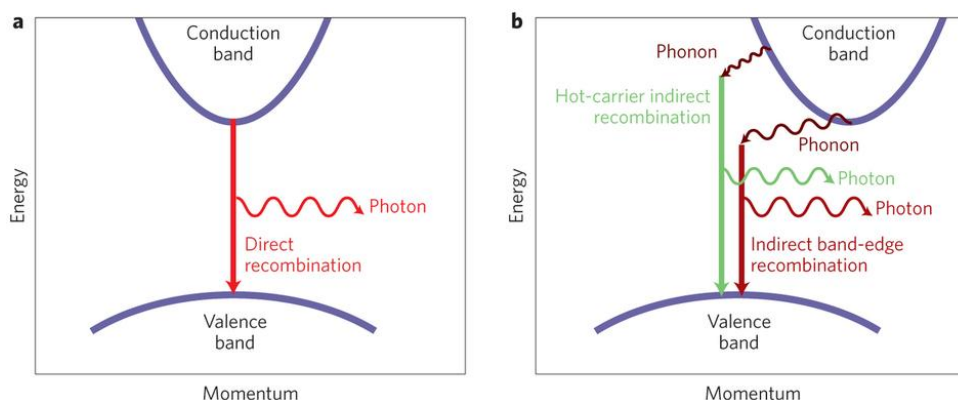


Fig. 2.3 Energy vs momentum diagram for (a) direct and (b) indirect band transition

http://www.nature.com/nphoton/journal/v7/n4/fig_tab/nphoton.2013.65_F2.html

When the momentum of electrons and holes in the conduction band and valence band is same then, it is called as direct band gap semiconductor. In which electron can transmit from the valence band to the conduction band, with the emission of photons. In an indirect band gap semiconductor, the electron must pass through an intermediate state and transfer momentum to the crystal lattice. In this process both a photon and a phonon are involved.

Simple parabolic bands absorption coefficient (α) is given by the following equation [50].

$$\alpha h\nu = A(h\nu - E_g)^n \quad 2.2$$

where, 'A' is a constant which is related to the effective mass associated with the valence and conduction bands, ' E_g ' is the optical band gap of the material, and 'n' assumes values of 1/2, 2, 3/2 and 3 for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively.

➤ Structural investigation technique

2.3.3 X-ray diffraction

X-ray Diffraction (XRD) study is used for the determination of the lattice parameters and crystal structure. It is non destructive, non contact technique which gives information about the composition, phases, crystal structure as well as crystallite size. The phenomenon of interaction of the X-rays with crystalline material is its diffraction, produced by the reticular planes that form the atoms of the crystal. Fig. 2.4 shows photographs of XRD instrument.

The interaction of incident rays and sample produces constructive interference when condition satisfies the Bragg's law, i.e.

$$n\lambda = 2d\sin\theta \quad 2.3$$

where, ' θ ' is incident angle, 'n' is the order of diffraction, ' λ ' is the wavelength of beam and 'd' is the spacing between diffracting planes. It shows the relationship between scattering angle, wavelength of radiation and the spacing between the planes of atoms. Since the distances between the atomic planes are dependent on the size and distribution of atoms.



Fig. 2.4 Photograph of X-ray diffractometry.

<http://www.iitr.ac.in/centers/IIC/uploads/File/XRD.pdf>

The position (θ) and intensity (I) of peak information are used to identify the type of material by comparing them with the Joint Committee for Powder Diffraction Standards (JCPDS) and to calculate the crystallite size (D). The Scherrer equation can be written as,

$$D = \frac{K\lambda}{\beta \cos \theta} \quad 2.4$$

where, 'D' is crystallite size, 'K' is a dimensionless shape factor, which is close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of crystallite. ' λ ' is the X-ray wavelength, ' β ' is the full width at half maxima (FWHM) in radians and ' θ ' the Bragg angle.

From the calculated crystallite size the micro strain (ε) and dislocation density (δ) were calculated by using following equation 2.5 and 2.6 respectively [51, 52].

$$\varepsilon = \frac{\beta \cos \theta}{4} \quad 2.5$$

where, 'ε' is micro strain, 'β' is full width at half maxima of prominent peak and 'θ' is Bragg angle.

$$\delta = \frac{1}{D^2} \quad 2.6$$

where, 'δ' is dislocation density and 'D' is crystallite size.

➤ Morphological investigation techniques

2.3.4 Field emission scanning electron microscopy

FESEM (Field Emission Scanning Electron Microscopy) is a microscope that works with electrons (particles with a negative charge) instead of light (Fig. 2.5). These electrons are liberated by a field emission source. The object is scanned by electrons according to a zig-zag pattern. A FESEM is used to observe very small topographic details on the surface. The FESEM technique is used to observe the morphology as small as 1 nm by the researchers in biology, chemistry and physics. The field emission source liberates the electrons and accelerated in a high electrical field gradient. The primary electrons are focussed and deflected by electronic lenses to produce a narrow scan beam. These narrow scan beam bombards the object, results in the secondary electrons are emitted from each spot on the object. The angle and velocity of these secondary electrons relate to the surface structure of the object. A detector catches the secondary electrons and produces an electronic signal. This signal is amplified and transformed into a scan image that can be seen on a monitor or to a digital image that can be saved and processed further. For the surface morphology study under FESEM instrument objects are first made conductive for current. This is done with gold or gold, palladium coating with an extremely thin layer (1.5 nm to 3.0 nm). The objects must be able to sustain the high vacuum and should not alter the vacuum, such as losing water molecules or gases. Then coating is performed in a separate device.

The incident electrons interact with specimen atoms and are significantly scattered by them (rather than penetrating the sample in a linear fashion). Fig. 2.6 shows the different types of interactions of the electron beam with the specimen. When the electrons are accelerated on materials (specimen) surface produces a number of interactions with atoms of the target material. These electrons undergo elastic and inelastic scattering without any interaction. Such a scattering produces

various signals that are used for imaging, quantitative and semi-quantitative information of specimen materials. The imaging includes secondary electrons (SE), backscattered electrons (BSE), cathodoluminescence (CL), auger electrons and characteristic X-rays. While, quantitative and semiquantitative analyses of specimens as well as element mapping typically employs characteristic X-rays.



Fig. 2.5 Photograph of FESEM instrument.

<http://www.51swave.com/upload/201105/1306464626.jpg>

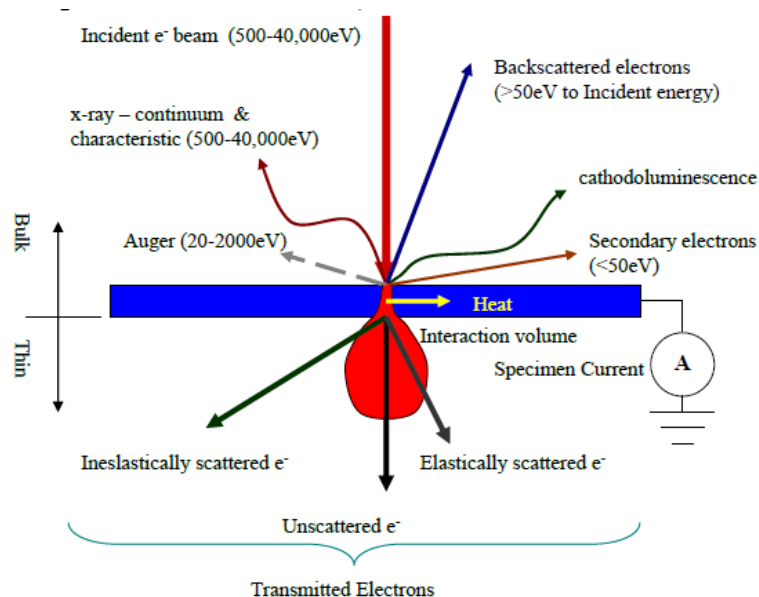


Fig. 2.6 Electron beam-specimen interaction.

<http://academic.uprm.edu/pcaceres/Courses/CHAMINA/HO5.pdf>

2.3.5 High resolution transmission electron microscopy

High resolution transmission electron microscopy (HRTEM) is providing higher resolution than the transmission electron microscope (TEM) that allows the imaging of the crystallographic structure of a sample. HRTEM can scan images with high resolution below 0.5 \AA at above 50 million times magnifications. Because of its high resolution and ability to determine the positions of atoms within the material, it has an important and powerful tool to study nanoscale properties of crystalline materials in material science. Fig. 2.7 shows photograph of HRTEM instrument. Samples for HRTEM study should be in the form of circular discs with 3 mm diameter. These could be either self supported or on a copper grid. The samples should have an electron transparent area with a thickness of around 100 nm or less, which gives better HRTEM images.



Fig. 2.7 Photograph of HRTEM instrument.

<http://www.dstuns.iitm.ac.in/microscopy-instruments.php>

The basic principle of HRTEM is similar to the optical microscope. The major difference is that in HRTEM, a focused beam of electrons instead of light, which is

used to achieve information about the structure and composition of material. A stream of electrons produced by the electron source named as a gun, which is accelerated towards the specimen using a positive electrical potential. This stream, then focuses using metal apertures and magnetic lenses called “condenser lenses” to obtain a thin, monochromatic beam. Beam strikes the specimen and a part of it gets transmitted through it. This portion of the beam is again focused using a set of lenses called “objective lenses” into an image. This image is then fed down the column, which produces enlarged image depending upon the magnification required through the “intermediate and projector lenses”.

A phosphor image screen is used to produce the image. The image strikes screen and light is generated, which enables the user to see the image. The darker areas of the image represent the thicker or denser region of the sample (few electrons were transmitted) and the lighter areas of the image represent those areas which are thinner/less dense (more electrons were transmitted). A main advantage of HRTEM analysis is that it can simultaneously give information in real space (imaging mode) and reciprocal space (diffraction mode) over the TEM analysis. From transmitted/diffracted electrons microscope records bright as well as dark field images inside the crystalline solid. Such an image pattern having information about crystal structure and defects associated with the sample. The HRTEM analysis provides,

- ✓ Examination of the microstructure at high resolution.
- ✓ Identification of phases.
- ✓ Determination of the crystal structure and orientation of the phases.
- ✓ Analysis of chemical composition of the individual phases.

➤ **Compositional analysis technique**

2.3.6 Energy dispersive X-ray spectroscopy

Energy dispersive X-ray spectroscopy referred as EDS or EDAX, is an analytical technique used to identify the elemental composition of materials and can be coupled with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). EDS provides elemental analysis on areas as small as nanometers in diameter.

The impact of the electron beam on the sample produces X-rays that are characteristic of the elements present in the sample (as shown in Fig. 2.8). The EDS analysis data displays the spectra showing peaks of corresponding elements provide the true composition of the sample. The elemental mapping of a sample and image analysis is also possible. The EDS becomes a powerful technique, particularly used in contamination analysis and industrial forensic science investigations. The EDS technique provides qualitative, semi quantitative, quantitative and spatial distribution of elements through mapping. The EDS technique is non destructive and specimens of interest can be examined in situ with no sample preparation.

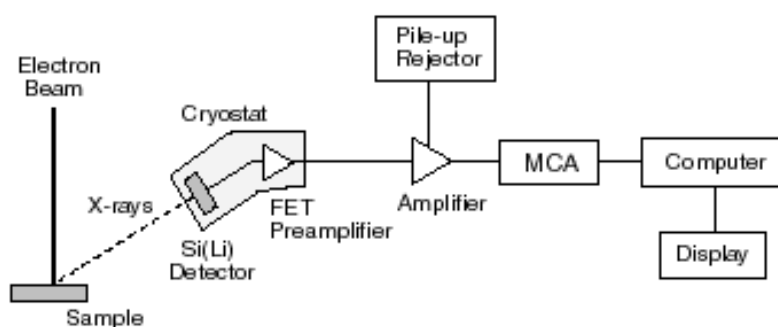


Fig. 2.8 Schematic representation of an energy dispersive X-ray spectroscopy.

<http://www.forensicevidence.net/iama/sem-edxtheory.html>

EDS systems include a sensitive X-ray detector, a liquid nitrogen Dewar for cooling and software to collect resultant spectra. The detector is mounted in the sample chamber of the main instrument at the end of a long arm, which is itself cooled by liquid nitrogen. The most common detectors are made of Si (Li) crystals that operate at low voltages, which improve the sensitivity. While, the new available detector technology, so called "silicon drift detectors" (Fig. 2.9) that operate at higher count rates without liquid nitrogen cooling. An EDS detector contains a crystal that absorbs the energy of incoming X-rays by ionization and yields free electrons in the crystal that become conductive, which produce an electrical charge bias. The X-ray absorption, thus converts the energy of individual X-rays into electrical voltages of proportional size, such an electrical pulse correspond to the characteristic X-rays of the element. EDS faces some limitations such as,

- ✓ The energy peak overlaps among the different elements, particularly those corresponding to X-rays generated by emission from different energy level

shells (K, L and M) in different elements. Particularly at higher energies, individual peaks may correspond to several different elements.

- ✓ EDS cannot detect the lightest elements, typically below the atomic number of Na.

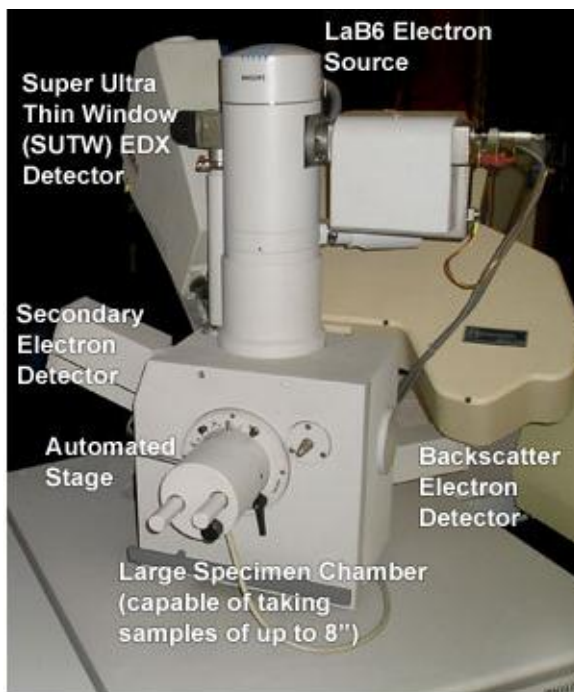


Fig. 2.9 Photograph of FESEM coupled with EDS instrument.

http://www.lpdlabservices.co.uk/analytical_techniques/sem/sem_instrument.php

2.3.7 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA) is based on the principle that X-rays hitting atoms generate photoelectrons (Fig. 2.10(a)). It is a typical example of a surface sensitive technique. Only electrons that are generated in the top few atomic layers are detected. XPS is used for investigation of surface characterization, which can analyze a sample to a depth of 2 nm to 5 nm. Kai Siegbahn, who won the Nobel prize in physics in 1981 for his research and development of XPS in the 1960. XPS reveals the chemical elements present at the surface and the nature of the chemical bond that exists between these elements. It can detect all of the elements except hydrogen and helium. It provides the following information from the top 10 nm of a sample.

- ✓ Elemental composition with up to 0.1 % sensitivity.
- ✓ Chemical state information.

- ✓ Surface chemical imaging with a resolution of 3 μm .
- ✓ Angle resolved XPS for the thickness and depth distribution of chemical species.
- ✓ Depth profiling using an ion gun to sputter away the surface during analysis.
- ✓ UV photoelectron spectroscopy (UPS) available in the same instrument provides information on the density of states in the valence band and electron work function.

Fig. 2.10(b) shows the schematic representation of working of XPS instrument. In a vacuum, surface is irradiated with X-rays (such as Al $K\alpha$ or Mg $K\alpha$). When an X-ray photon hit and transfers this energy to a core level electron. It is emitted from its initial state with a kinetic energy, which is dependent on the incident X-ray and the binding energy of the atomic orbital from which it originated. The energy and intensity of the emitted photoelectrons are used to identify and determine the concentrations of the elements. These photoelectrons originate from a depth of <10 nm therefore the information obtained is from within this depth. For XPS, these are 'soft' X-rays of 200 eV to 2000 eV photon energy, although the X-rays are usually monochromated.

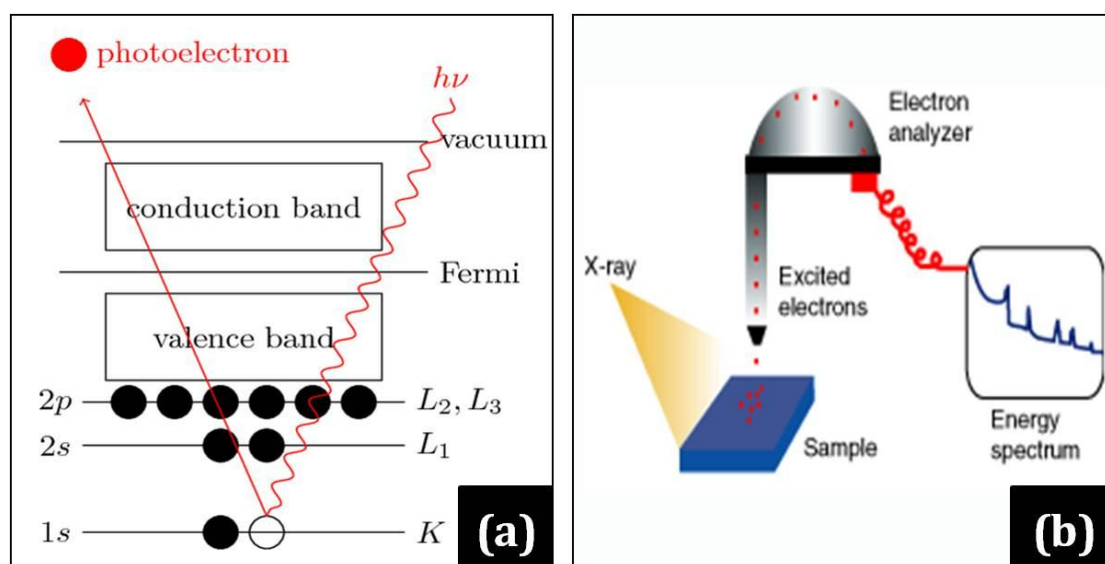


Fig. 2.10 (a) Production of photoelectron and (b) schematic for working of XPS.

<http://www.texample.net/tikz/examples/principle-of-x-ray-photoelectron-spectroscopy-xps/>

<http://www.lanl.gov/orgs/nmt/nmtdo/AQarchive/04summer/XPS.html>

This means that the emitted photoelectrons have a particular kinetic energy (E_k) which is measured by a detector. E_k can be related to the binding energy (E_B) of the electron in the solid. The binding energy with the kinetic energy of core electron is given by the Einstein relationship: [53]

$$h\nu = E_b + E_k + \phi \quad 2.7$$

$$E_b = h\nu - E_k - \phi \quad 2.8$$

Where, ' $h\nu$ ' is the X-ray photon energy, ' E_k ' is the kinetic energy of photoelectron and ' ϕ ' is the work function induced by the analyzer, about ~4 eV to 5eV. The ϕ can compensate artificially and eliminated by giving the binding energies as follows,

$$E_b = h\nu - E_k \quad 2.9$$

Therefore, the binding energy is a direct measure of the energy required to remove the electron from giving electronic level to the Fermi/vacuum level of free atom/molecules. This is what gives XPS the power to measure not only elemental information, but also relate the peak intensity of the element within the sample.



Fig. 2.11 Photograph of XPS instrument.

<http://www.nottingham.ac.uk/nnnc/research/xps/xps.aspx>

The oxidation state and chemical environment influence on the exact binding energy of the elements. The higher oxidation state atoms show higher binding energy

because of the extra Coulombic interaction between the photoemitted electron and ion core. The ability to discriminate between different oxidation states and chemical environments, which is the one of the major strength of the XPS technique. Fig. 2.11 shows photograph of XPS instrument.

➤ Electrical characterization techniques

2.3.8 (A) Electrical conductivity measurement

The electrical conductivity (EC) of the synthesized materials can be measured by using DC two point probe method. Fig. 2.12(a,b) shows photograph and schematic representation of the EC measurement unit. The two brass plates of the size $10 \times 5 \times 0.5$ cm are grooved at the center to fix the heating elements. To maintain uniform temperature two brass plates were screwed to each other. A mica sheet was placed between film and brass plate to avoid contact between film and brass plate. The silver paste was applied to ensure good electrical contact between films and probe. The chromel-alumel thermocouple fixed at the center of the brass to record the working temperature. Testronix model 34C (power supply unit) was used to pass the current through the sample. The potential drop across the film was measured with the help of MECO 801 digital multimeter and the current passed through the sample was noted with a sensitive 4 digit picoammeter (Scientific equipment, Roorkee DPM 111). The measurements were carried out by keeping the film system in a tight box, which was kept at room temperature.

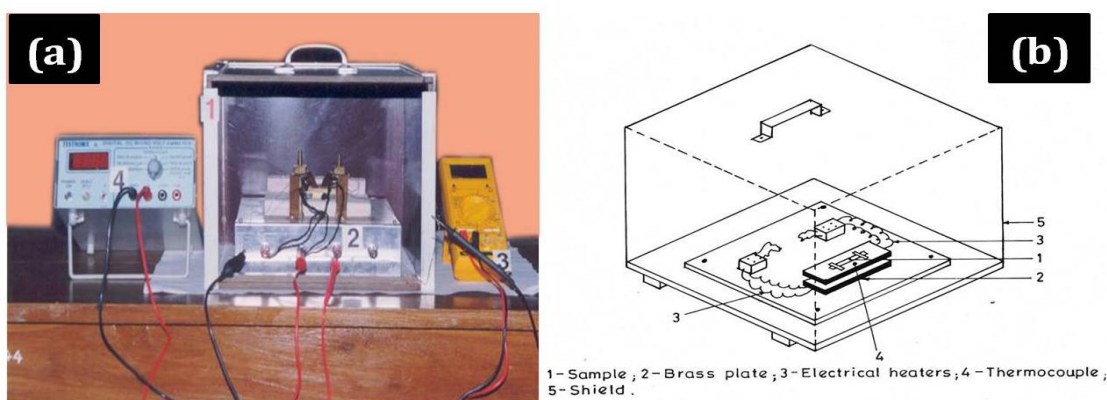


Fig. 2.12 (a) Photograph and (b) schematic representation of the electrical EC measurement unit.

2.3.8 (B) Thermoelectric power measurement

Fig. 2.13(a,b) shows photograph and schematic representation of the thermoelectric power (TEP) measurement unit. In TEP measurement unit one junction maintained at a higher temperature than the other by applying metal contacts at the ends of semiconductor film and a potential difference is developed between two electrodes and the thermoelectric/Seebeck voltage is produced due to,

- ✓ The majority of charge carriers diffuses from hot to cold junction in a semiconductor, develops a potential difference between the specimen.
- ✓ The other part which contributes to the thermoelectric voltage is the contact potential difference between metal and semiconductor at two junctions.

In TEP measurement apparatus two brass blocks were used for measurement process. Out of one used for sample holder as well heater and other brass block used was kept at room temperature. Insulated barrier was used to maintain thermal isolation of cold and hot junction. The size of the film used for measurement was 40 mm x 12.5 mm x 1.35 mm, were fixed on two brass blocks. The temperature sense was obtained by using Chromel-Alumel thermocouple (24 gauze). A 65 watt strip heater was used for heating the sample. The temperature of the hot junction was raised slowly from room temperature, with a regular interval of 10 K. Silver paste was applied for contact. A backlit box was used for proper shielding of the TEP unit, which also minimizes to some extent, thermal radiation losses.

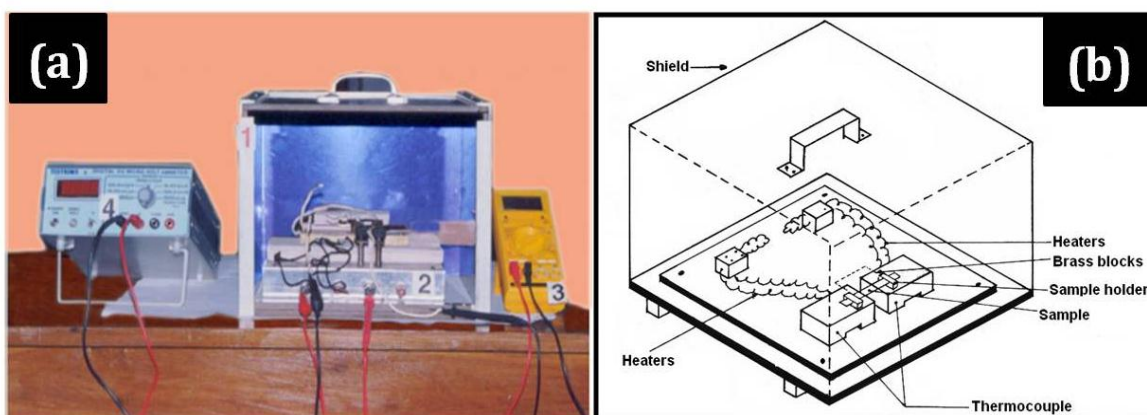


Fig. 2.13 (a) Photograph and (b) schematic representation of the TEP measurement unit.

➤ Photoelectrochemical characterization

2.3.9 (A) Introduction of solar cells

French physicist A. E. Becquerel recognized first photovoltaic effect in 1839. Charles Fritts builds first solar cell coated semiconducting selenium with an thin layer of gold to form the junctions in 1883. In 1954 Bell laboratories experimenting with semiconductor and accidentally they found that silicon doped with certain impurities was very sensitive to light. Daryl Chapin, Calvin Fuller and Gerald Pearson, were invented the first practical device for converting sunlight into useful electrical power. A result in the production of the first practical solar cells with the energy conversion efficiency is of about 6 %. A solar cell is a semiconductor device that directly converts solar energy into electricity.

In 1970, Mobil, RCA, Sandia, Westinghouse, ARCO and co-workers had obtained efficiencies in the 14 % to 17 % range. Typical solar cell parameters were V_{oc} of 600 mV to 645 mV, J_{sc} of 34 mA/cm² to 37 mA/cm² and a fill factor of 77 % to 82 %. However, surface passivation was poor with low bulk lifetime due to the contamination during ingot growth or cell fabrication. During the 1980s and early 1990s a sustainable improvements in cell efficiencies reported by various laboratories, at the University of New South Wales, Austria and at Stanford University, USA. This is illustrated in the chart of best solar cell efficiencies maintained by the NREL, which is shown in Fig. 2.14.

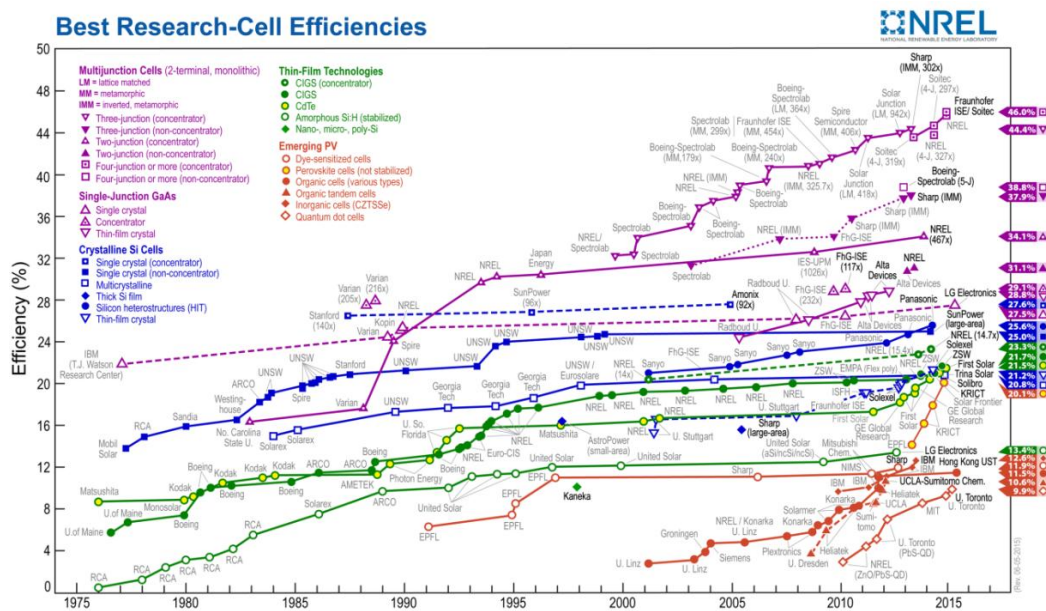


Fig. 2.14 Best solar cell efficiencies chart.

http://en.wikipedia.org/wiki/Photovoltaics#/media/File:Best_Research-Cell_Efficiencies.png

The solar cell is a device that generates electricity directly from sunlight by means of photovoltaic effect. Solar energy increasingly used in resources in different areas such as,

- ✓ Fuel production.
- ✓ Agriculture and horticultures.
- ✓ Urban planning and architecture.
- ✓ Heating, cooling and ventilation.
- ✓ Electricity generation.

The electricity is generated in two ways by solar energy,

- **Thermal solar energy**

In this case solar energy for heating fluids, this can be used as a heat source or to run turbines to generate electricity.

- **Photovoltaic solar energy**

Electricity is generated by solar energy using photovoltaic phenomenon.

The basic steps in the operation of a solar cell are (Fig. 2.15),

- ✓ The generation of light generated carriers.
- ✓ The collection of the light generated carries to generate a current.
- ✓ The generation of a large voltage across the solar cell.
- ✓ The dissipation of power in the load and in parasitic resistances.

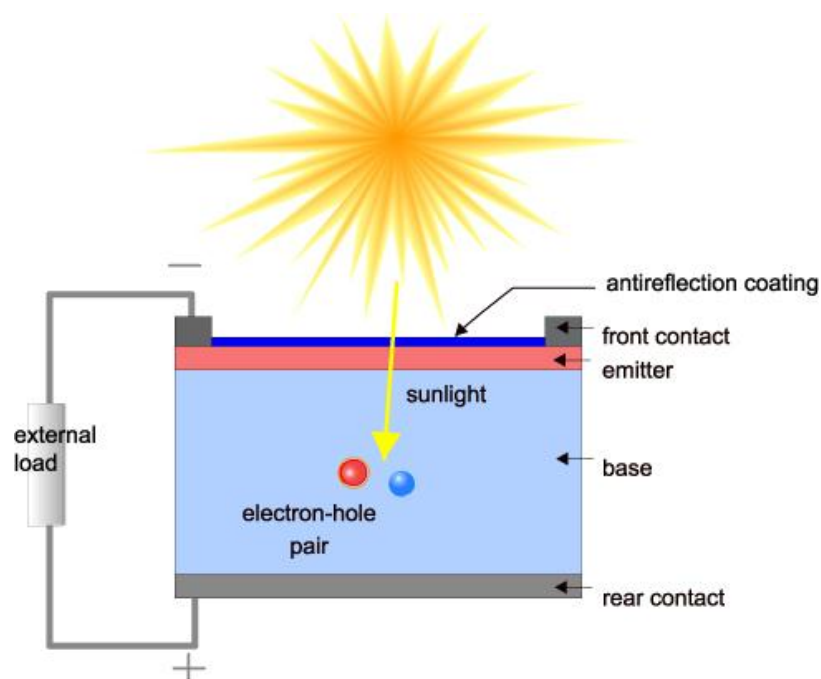


Fig. 2.15 Schematic of basic working operation of solar cell.

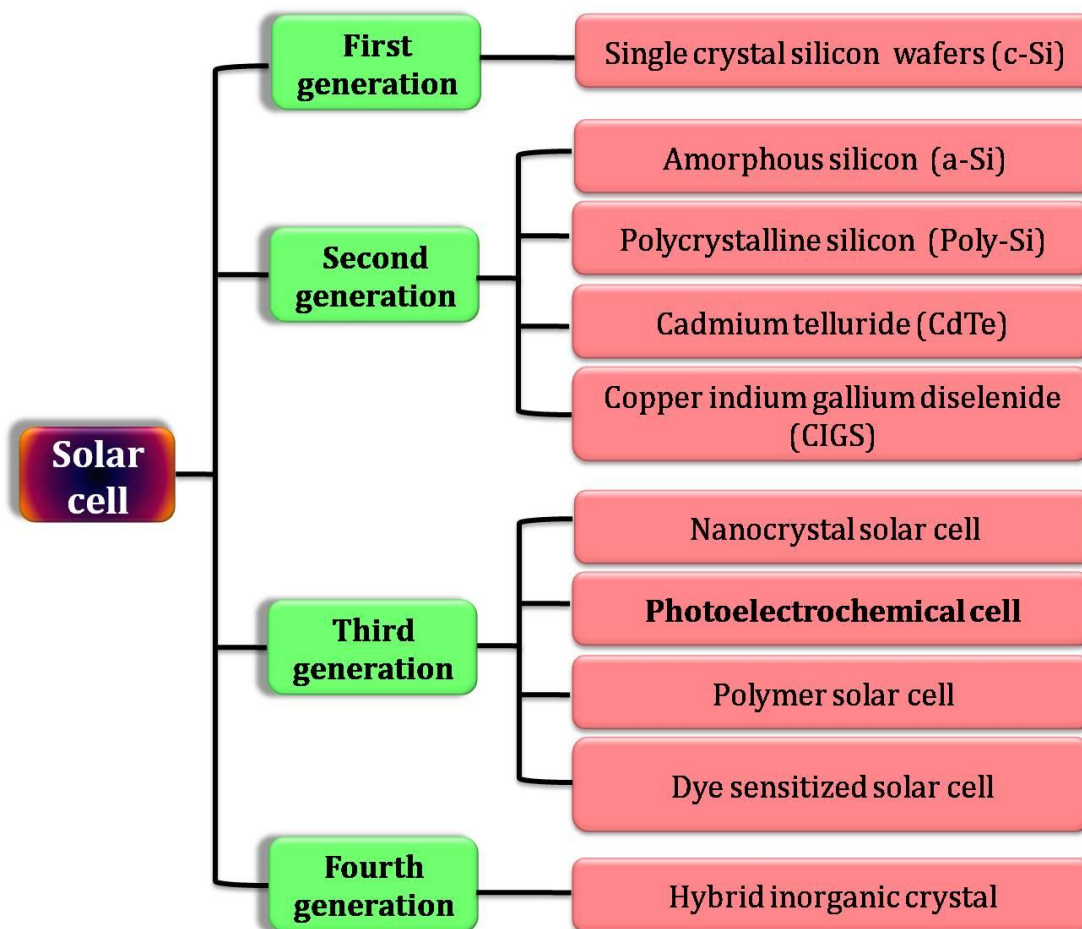
<http://www.pveducation.org/pvcdrom/solar-cell-operation/solar-cell-structure>

2.3.9 (B) Solar cell generations

First generation

Basically, solar cell generations are divided into four parts (Table 2.3). First generation solar cells are nothing but a single crystal silicon wafer and typically demonstrate a performance about 15 % to 20 %. These types of solar cells dominate the market and those are mainly used in routine life. The benefits of this solar cell technology lie in their best performance with their high stability. However, they are rigid and require a lot of energy production.

Table. 2.3 Solar cell generations.



Second generation

Second generation solar cells are called thin film solar cells because they are based on amorphous silicon or non silicon materials such as cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS), where the typical performance is 10 % to 15 %.

Thin film solar cells use layers of semiconductor materials only a few micrometers thick. Second generation solar cell avoid the use of silicon wafers based materials and lowers materials consumption to reduce production costs compared to the first generation. However, in second generation solar cells include vacuum processes and high temperature treatment results in the large energy consumption in the production of these solar cells.

Third generation

Currently lots of research is going into the third generation of solar cell (nothing but new generation). This generation of solar cell made a variety of new materials rather than silicon cell such as, nanotubes, wires, solar inks using conventional technologies, organic dyes and conducting plastics. The main aim of this generation is to improve solar cell efficiency over a wide band solar energy compared to solar cell already available commercially. Nowadays, most of the work on third generation solar cells is being done in the laboratory and being developed by new companies and for the most part is not commercially available. Despite the performance and stability of third generation solar cells is still limited compared to first and second generation solar cells having great potential and are already commercialized. In addition to this research interest in polymer solar cells has increased significantly in recent years.

The research on organic photovoltaic (OPVs) solar cell started as early as the 1950s, when simple organic dyes, like chlorophyll or magnesium phthalocyanines, were investigated. Output power conversion efficiencies (PCE) were surpassing i.e. 0.1 % [54]. This was attributed to the fact that upon illumination formed excitons (localized and bound electron-hole pairs), does not get dissociate readily in organic semiconductors. From this it concluded that, the main weakness of single layer architectures was the charge recombination.

Considering these facts, in 1986 Tang used a two component donor-acceptor active layer, consisting of a copper phthalocyanine (donor) and a perylene derivative (acceptor). It was observed that, exciton dissociation at the heterojunction (interface) of the two molecules was due to the substantially different electron affinities and ionization potentials. This results into 1 % conversion efficiency [55]. Fig. 2.16 represents the working principle and device structure of organic solar cell.

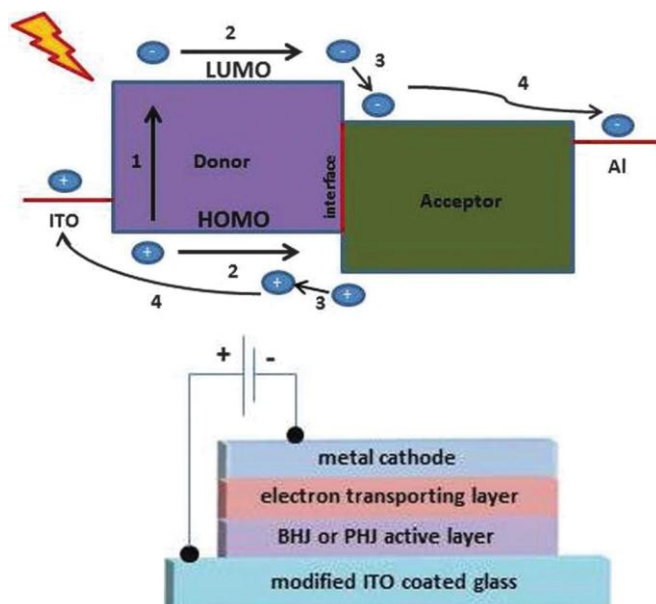


Fig. 2.16 Working principle and device structure of organic solar cell.

<http://pubs.rsc.org/en/content/articlepdf/2015/cc/c4cc09888a>

In the 1990s opened new horizons in the area of photovoltaics i.e. dye sensitized solar cells (DSSCs) and entered dynamically the race for the cost efficient device [56]. It has been shown great potential as an alternative to standard silicon solar cell and the obtained efficiencies, growing from 7 % in the seminal report to 13 % recently [57]. In DSSCs, tremendous technological progress is focused for tailoring their different properties for successful device architecture. Out of these main three components of the cell requires fine tuning, i.e. the organic dye, the semiconductor materials with nanocrystalline nature and the redox electrolyte couple. The working principle of DSSCs is different than that of OPVs. It includes (as shown in Fig. 2.17),

- ✓ Photoexcitation of the sensitizer.
- ✓ The injection of electrons into the conduction band of the metal oxide (Ex. TiO_2).
- ✓ Electron transport to the working electrode.
- ✓ Regeneration of the oxidized dye by electron donation from the redox couple of the electrolyte.

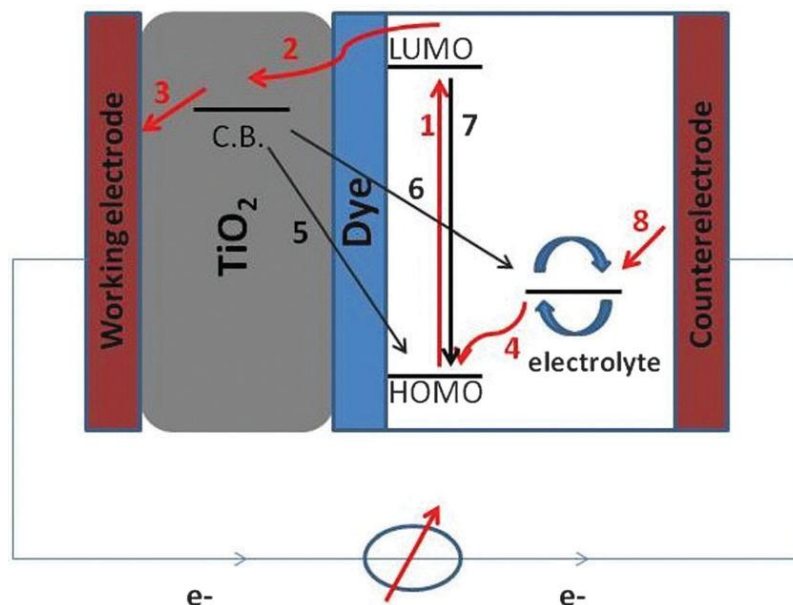


Fig. 2.17 Working principle of DSSCs.

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The sensitizer is the key element in DSSCs. It governs the photon harvesting, charge generation and charge transfer processes. Thousands of photosensitizers have been developed and ruthenium based photosensitizers particularly N3, its salt analogue N719, N749 marked a significant breakthrough [58-60]. These particular dyes have showed PCE reaching up to 10 % to 11 % and incident photon to current conversion efficiency (IPCE) of 80 % across the visible part of the solar spectrum. Thermal, photostability and excellent charge transfer properties make ruthenium dye more interesting and promising dye for DSSCs device application.

Fourth generation

Fourth generation solar cells are considered the future of solar technology. This group brings most successful category of solar cells for mankind and those were hybrid nanocrystal cells. This hypothetical generation of cell polymers and nanoparticles were mixed to make a layer which can help electrons and protons to move for producing a better voltage and good quality of direct current.

2.3.9 (C) Requirements of photoelectrochemical cells

The basic requirements of PEC cells are a redox electrolyte, a semiconductor photoelectrode and a counter electrode.

A redox electrolyte

The photoelectrochemical performance and the efficiency of PEC cell depends on the properties of a redox electrolyte. The proper choice of an electrolyte is very important. An electrolyte redox couple should possess following properties,

- ✓ It should be cost effective and non toxic.
- ✓ Redox potential should match with fermi level of a photo electrode.
- ✓ It should be transparent to incident light photons.
- ✓ The redox reactions should be diffusing limited and stable for the long duration under illumination.
- ✓ It should not chemically react with photoelectrode material.

The formal redox potentials of the different electrolytes were studied with references to that the suitability of electrolyte. A suitable electrode was selected by determining λ_{\max} of various electrolytes such as, iodide/polyiodide (I^-/I_3^-), ferricyanide/ferrocyanide (Fe^{3+}/Fe^{2+}), sulfide/polysulfide (S^{2-}/S_2^{2-}) solution. The absorption cutoff of iodide/polyiodide (I^-/I_3^-), ferricyanide/ferrocyanide (Fe^{3+}/Fe^{2+}) was observed between 500 nm to 850 nm. However, the polysulfide solution was found to be suitable and it shows absorption, cut off in the visible (~ 390 nm) range of spectra. The sulfide/polysulfide couple with formal redox potential -0.70 V vs standard calomel electrode (SCE) ± 0.005 V. It means that the polysulfide redox electrolyte shows optical absorption in the visible region of the solar spectrum and found suitable for constructing PEC cell of ternary/quaternary/multinary thin films [61, 62]. The formal redox potentials of the various electrolytes are shown in Table 2.4.

Table 2.4 The formal redox potentials of various electrolytes used for construction of PEC cells.

Sr. No.	Redox electrolyte	Formal redox potential (V)
1	Iodide/polyiodide couple	-0.32 V Vs SCE ± 0.005 V
2	Potassium ferricyanide /potassium ferrocyanide	-0.365 V Vs SCE ± 0.005 V
3	Sulfide /polysulfide couple	-0.72 V Vs SCE ± 0.005 V

A semiconductor photoelectrode

A semiconducting photoelectrode material should satisfy the following conditions,

- ✓ It should be a direct band gap type with a high optical absorption coefficient.
- ✓ The band gaps should be utilized, the maximum span of the solar spectrum.
- ✓ The minority carrier diffusion length and the depletion layer width should be large.
- ✓ The material should be stable against photo dissolution and photocorrosion in a redox electrolyte.
- ✓ The charge carriers should have high mobility and lifetime.
- ✓ The material should be thick enough to absorb all the incident radiations.
- ✓ Contacts to the semiconductor material should be Ohmic.
- ✓ The cost of the basic material and manufacturing processes should be low.

A counter electrode

At the counter electrode, electrolyte species are oxidized and it does not give any chemical change in composition of the electrolyte. It should have following properties,

- ✓ It should be stable in the electrolyte.
- ✓ When a counter electrode is immersed in an electrolyte, the half cell potential of the electrode should match with that of the half cell potential of semiconductor electrode.
- ✓ It should be chemically inert and electronically active.
- ✓ The counter electrode should have a low potential for the reduction reaction.

2.3.9 (D) Efficiency of photoelectrochemical cells

The ratio between the maximum power generated and the product of J_{sc} and V_{oc} is known as fill factor (FF). The FF is calculated using equation (2.10) as follows,

$$FF = \frac{J_{max} V_{max}}{J_{sc} V_{oc}} \quad 2.10$$

Higher value of FF gives better quality of the solar cell device. The short circuit current (J_{sc}) is the current produced when the positive and negative terminals of a cell are short circuited and the voltage between the terminals is zero, at the load resistance of zero. The open circuit voltage (V_{oc}) is the voltage across the positive and

negative terminals under open circuit conditions and current is zero, at the load resistance of infinity. The conversion efficiency (η) is the percentage of power converted (from absorbed light to electrical energy) and collected, when a solar cell is connected to an electrical circuit. The efficiency is calculated using the following equation (2.11). Fig. 2.18 shows the ideal current density-voltage (J-V) curve.

$$\eta = \frac{J_{sc} V_{oc}}{P_{in}} \times FF \times 100 \quad 2.11$$

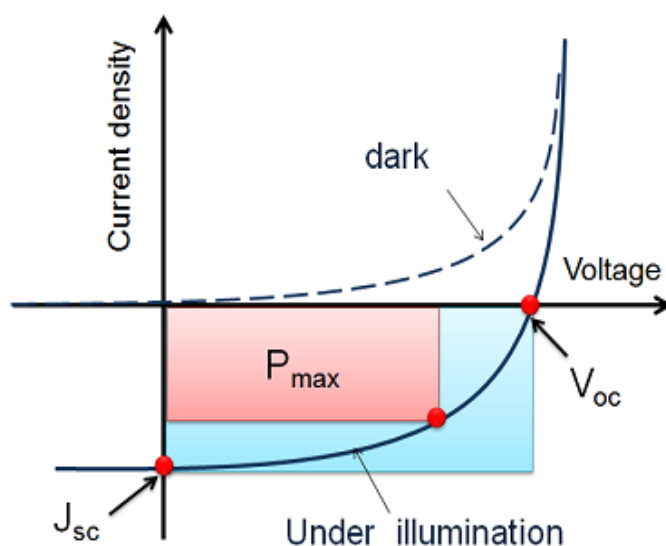


Fig. 2.18 Ideal current density-voltage (J-V) curve.

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