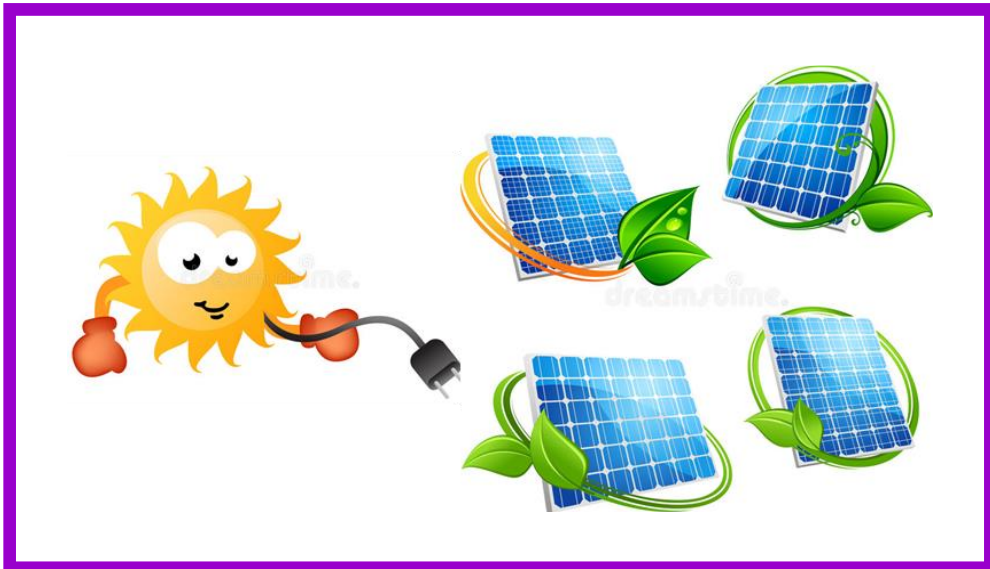


Chapter 1

Chapter 1

General Introduction



1.1 Introduction

In the modern era, the energy sources become most important part of the human life. The use of technology is increasing with efficient rate day by day and growing the industrial energy demands due to which, the consumption of energy will be enhancing with the time. Nowadays, the non-renewable energy sources such as coal, nuclear power, petroleum and natural gas are used to fulfill the maximum energy demands. However, due to the limited availability, the energy demands are hardly expected to fulfill by these sources in the near future. And these sources also producing the major contributors, enhancing the global warming. These shortcomings of non-renewable energy sources may be resolved by using the renewable energy sources. There are different kinds of renewable energy sources available such as solar photovoltaics, hydro-power, wind power, solar heater, solar concentrator, biomass, biofuel, wave power, and tidal power. Amongst them, the energy from solar photovoltaic sources is expected to key role in the near future.[1,2] The largest renewable power source of our systems is solar irradiation. The total energy received from Sun at earth's surface is estimated to be 1.2×10^5 TW every year, which is about 6000 times more than the present human power consumption. For the efficient utilization of the solar energy, a practical system is required for the photo-conversion, storage and distribution of this energy.

1.2 Background and Development of Photovoltaics

1.2.1 Solar Radiation

Solar radiation is an electromagnetic energy emitted by the Sun due to the nuclear fusion reaction occur inside its core. Even through very hot on the inside, the temperature gradually decreases towards the surface, from where the emission occurs. The surface temperature is estimated to be

about 5800 K. At this temperature, the solar spectrum resembles the spectrum of a black body at 5800 K, and emits EM radiations covering the entire EM spectroscopy including the ultra violet (UV), visible infrared, x-ray, and radio waves. The spectrum of solar radiation on the Earth’s surface with and without absorption of some wavelengths by the atoms and ion in atmosphere are shown in **Figure 1.1**.

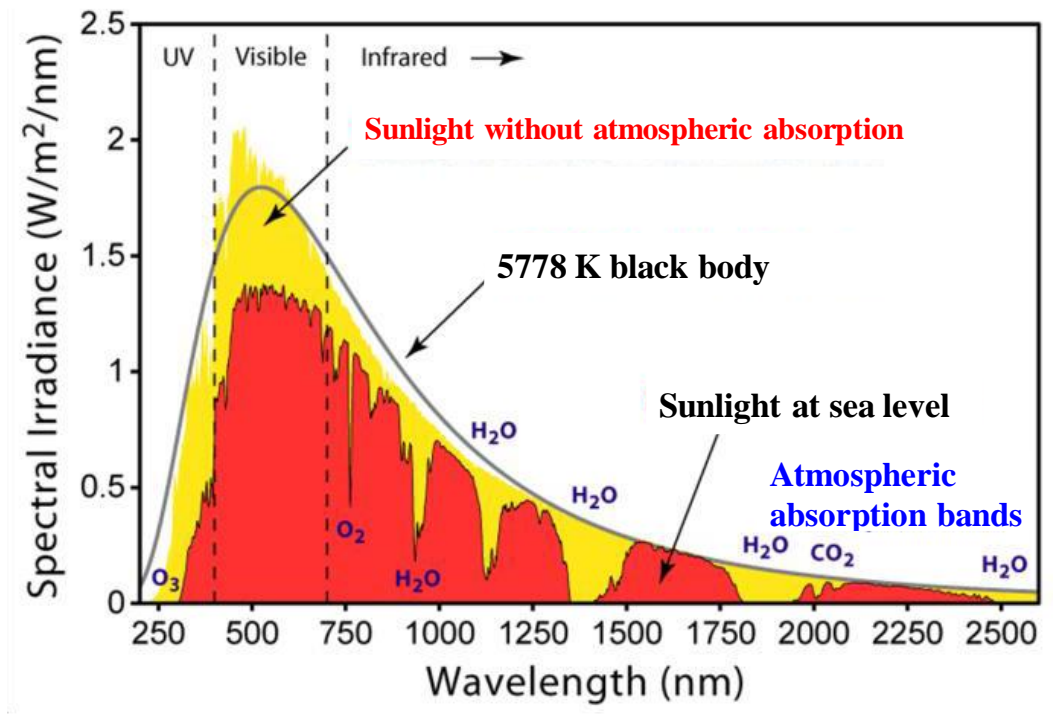


Figure 1.1: Solar radiation spectrum on the Earth’s surface.[3]

The power density of Sun illumination falls on object defined in terms of *solar irradiance* (H_0) and its SI unit is W/m^2 . The solar irradiance (H_0) is the ratio of the total power emitted from the Sun’ surface and the distance (D) between the Sun and object. The solar irradiance is measure by the using the following equation (1.1).

$$H_0 = \left(\frac{R_{Sun}^2}{D^2} \right) H_{Sun} \dots \dots \dots (1.1)$$

where, R_{Sun} is the radius of the sun in meters, D is the distance between the object and Sun in meters, and H_{Sun} is the power density at Sun's surface in W/m^2 .

The distance between Sun and Earth surface is defined by International Astronomical Union (IAU) as 148597870700 meters and the solar radiation is found to be approximately $1366.1 W/m^2$ by using the above equation (1.1).

Table 1.1: The distance between the various planet and Sun and the solar irradiance on the respected surfaces.

S.N.	Planet	Distance ($\times 10^9$ meters)	Mean Solar irradiance (W/m^2)
1.	Mercury	57	9116.4
2.	Venus	108	2611.0
3.	Earth	150	1366.1
4.	Mars	227	588.6
5.	Jupiter	778	505
6.	Saturn	1426	15.04
7.	Uranus	2868	3.72
8.	Neptune	4497	151
9.	Pluto	5806	0.878

1.2.2 Air Mass

Air mass is the measurement of reduction of the power of the sunlight is due to absorbed by the atmospheric components such as dust and air. AM is the path length travelled by the light via

atmosphere relative to the length of the shortest possible pathway (Sun directly top on our head) of the light. The AM is calculated by the following relationship (Equation 1.2).

$$AM = \frac{1}{\cos \theta} \dots \dots \dots (1.2)$$

where, θ represent the angle of light from the vertical position and it is known as elevation angle or zenith angle. The value of AM is dependent on the elevation angle, if $\theta = 0^\circ$, then AM value is maximum that means the light travelling with the shortest possible path length.[4] AM 1.5G is used as a standard spectral distribution at the surface of the Earth (G stands for global, and includes both the diffuse and direct radiation), and AM 1.5D is used for direct radiation only. For AM 1.5G, $\theta = 48.2^\circ$ and the difference of the path length of the light is 1.5 times higher than that of AM 1.5.

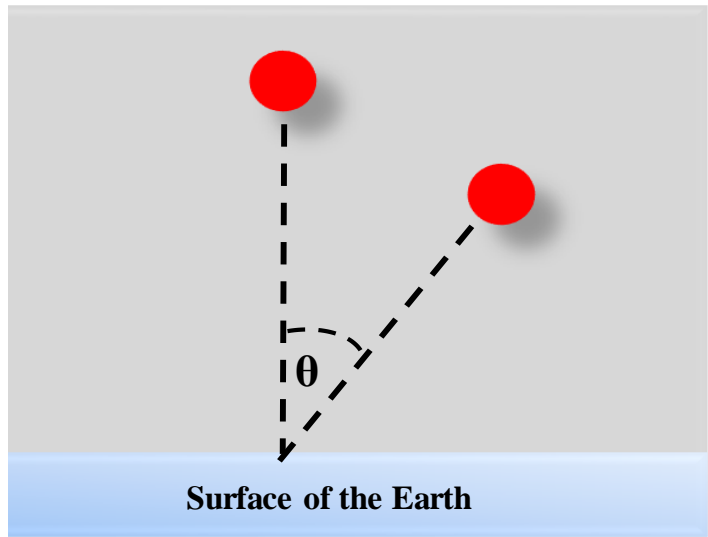


Figure 1.2: Air mass calculated from the zenith point.

The solar irradiance value is 970 W/m² for AM 1.5G, however for convenience, this standard global spectrum is normalized to 1 kW/m² and accepted as standard 1 Sun illumination at the Earth’s surface. Consequently, 1 kW/m² is used in solar simulators to record the performances of solar cells in laboratories.

1.2.3 History and Development of Photovoltaics

The term *photovoltaics* is defined as the, the solar energy (*Photo-*) is directly converted in electricity (*-voltaic*), such conversion takes place through a device is known as photovoltaics (PV) device and the whole process is based on the *photovoltaic effect*. The *photovoltaics effect* was first recognized by the French physicist Alexandre-Edmond Becquerel in 1839, and discover the first PV cell, which is also known as Becquerel effect.[5] The photo-electrochemical cell was prepared by immersing platinum electrode in an electrolyte comprising silver chloride in an acidic medium.

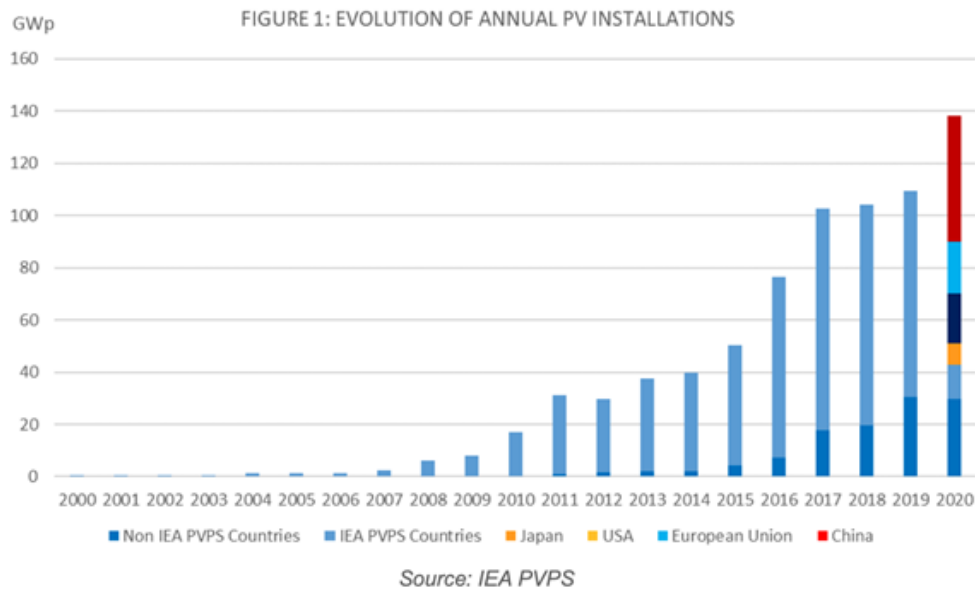


Figure 1.3: World's photovoltaic market growth. (Source: IEA PVPS)

These fabricated cells were also produced the electric current and under irradiation of light. In 1954, the Bell laboratories was first invented the practical silicon based PV cell and the PV technology was jump by for this invention, and the cell power conversion efficiency 6 % was observed.[6] Since then, a steady growth of the PV industries has afforded subsidized electrical energy in urban areas as an on grid and off grid technology. Since then, the continuous growth of

PV technology taking places and PV technology gives the subsidized electrical energy in urban areas via on-grid and off-grid technology. The global expansion of the PV industries over the last two decades can be understood from the snapshot PV: 2020 released by International Energy Agency.

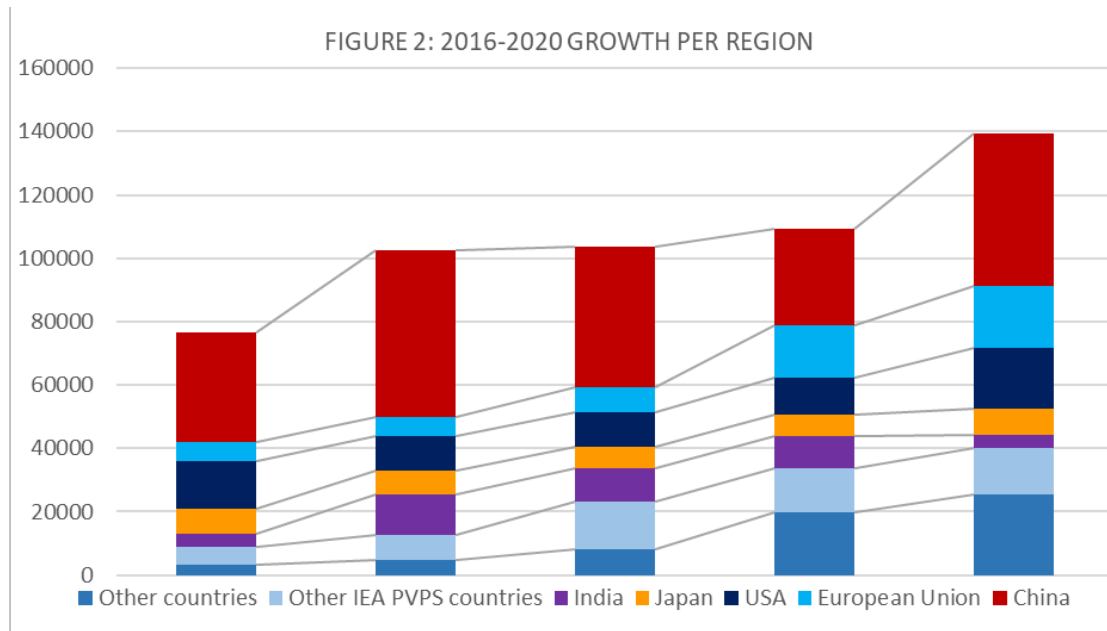


Figure 1.4: Growth per region of the world’s photovoltaic market 2016-2022.

According to this report, at least 20 countries installed more than 1 GW, 14 countries have more than 10 W of total cumulative capacity, five have more than 40 GW. China alone represented the 253.4 GW by the European Union (as EU27), which used to lead the rankings for years and ranks second since 2015 (151.3 GW), the USA ranks third (93.2 GW) and Japan fourth (71.4 GW). In 2020, the total installed was 744.6 GW by the IEA PVPS countries and other remaining other market are also installed the 15.8 GW, the total cumulative installed capacity to around 760.4 GWdc. The last year (2020) major growth of the PV market was coming from China. The PV market changing dynamics and the higher influence of the Chinese PV market was shown in the

Figure 1.4, and the major countries display the continuous growth of PV market in 2020. Hence, the COVID-19 pandemic did not significantly impact on PV market development in 2020.

1.2.4 Shockley-Queisser Limit

The performance of the solar cell is based on the efficiency conversion of the incident light in to electricity. The performance of the solar cell is highly depending upon the properties of the semiconductor materials The Shockley-Queisser limit (*SQL*) is the maximum theoretical efficiency of solar cell which is calculated by examining the amount of electrical energy is generates by single incident photon.

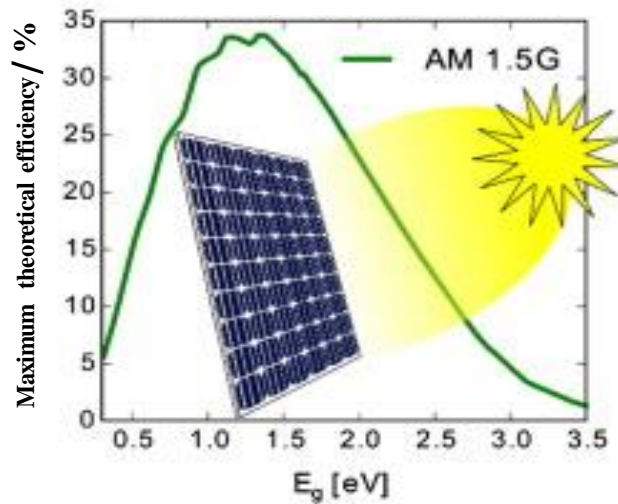


Figure 1.5: Variation of the Shockley-Queisser Limit with band gap of various semiconductor materials.[7]

In 1961, William Shockley and Hans Queisser was first introduced the concept of the maximum theoretical efficiency of the solar,[8] which is made by single p-n junction and they calculated that the maximum theoretical efficiency around 33.7 % for the single p-n junction solar cell under 1 sun (AM 1.5) solar illumination, that means, the ideal p-n junction solar cell will produce the

power density 337 W/m^2 with 1 sun (1000 W/m^2) solar irradiation. The **Figure 1.5** shows the *SQL* is the function of the band gap.[7] The most common materials which are used in the PV cell is silicon and the silicon with band gap 1.1 eV shows the theoretical efficiency limit around 32 % while, the practical monocrystalline silicon based solar cell exhibited the approximately 24 % power conversion efficiency.

1.3 Classification of Solar Cells

Nowadays, the area of photovoltaics becomes broad and a variety of solar cells was developed rather than traditional silicon based solar cells. Depending upon the materials used in device fabrication and structure of device the solar cells are generally classified in to three generations.

1. **First Generation:** Solar cell based on crystalline silicon semiconductor, silicon semiconductor materials are used to fabricate the PV devices and further it can be divided in to two types: (a) monocrystalline and (b) polycrystalline silicon solar cells.
2. **Second Generation:** PV device are based on thin film technology. The most important semiconductor materials used in second generation PV devices are amorphous silicon, copper indium gallium selenide (CIGS) and cadmium telluride.[9,10]
3. **Third Generation:** These types of PV devices are potentially able to overcome the Shockley-Queisser limit of 31-41 % power conversion efficiency for single band gap solar cells. The emerging PV system are:[11-17]
 - (a) Organic solar cell,
 - (b) Dye sensitized solar cell,
 - (c) Quantum dots sensitized solar cell, and
 - (d) Perovskite solar cell.

The PV devices can also have classified in two sections based on their working principles

- (1) **Conventional p-n Junction Solar Cells.** In which types of PV devices, the inorganic semiconductor materials are absorbing the sunlight and electrons are exciting across the semiconductor band gap. The first- and second-generation solar cell based on these working principles.
- (2) **Excitonic Solar Cells.** In these types of solar cells, the sunlight is absorbed by: a polymer, a dye molecule, a quantum dots, and a perovskites material to generate the electron-hole pair (exciton). This exciton is dissociating on hetero-interface and produced the charge carries.

1.3.1 Conventional p-n Junction Solar Cells

To produce the electrical energy from the solar energy through photovoltaics devices there are three essential processes carried out:

- (a) absorption of solar energy in term of photon,
- (b) formation of exciton (electron hole pair) and further separation of exciton,
- (c) collection and extraction of free carriers via two electrodes.

The conventional p-n junction solar cell band diagram under irradiation of solar light is shown in Figure 1.6. The light penetration is directly intensity of light. The photons having sufficient amount of the energy can excite the electron from valence band to the conduction band of the semiconductor and creating a positive vacancy in valence band which is known as holes. If the exciton (electron-hole pair) is generated in depletion region, the electron is move toward n-side and holes move toward p-side is due to the presence of electric field in depletion region resulting, the charge separation take places. And the electron-hole pair also generates p-side and n-side (in outside the depletion layer). These generated electron-hole are diffuse in the space charge region

and contribute to the output current. Finally, the separated charge carriers are collected at the surfaces two electrode.

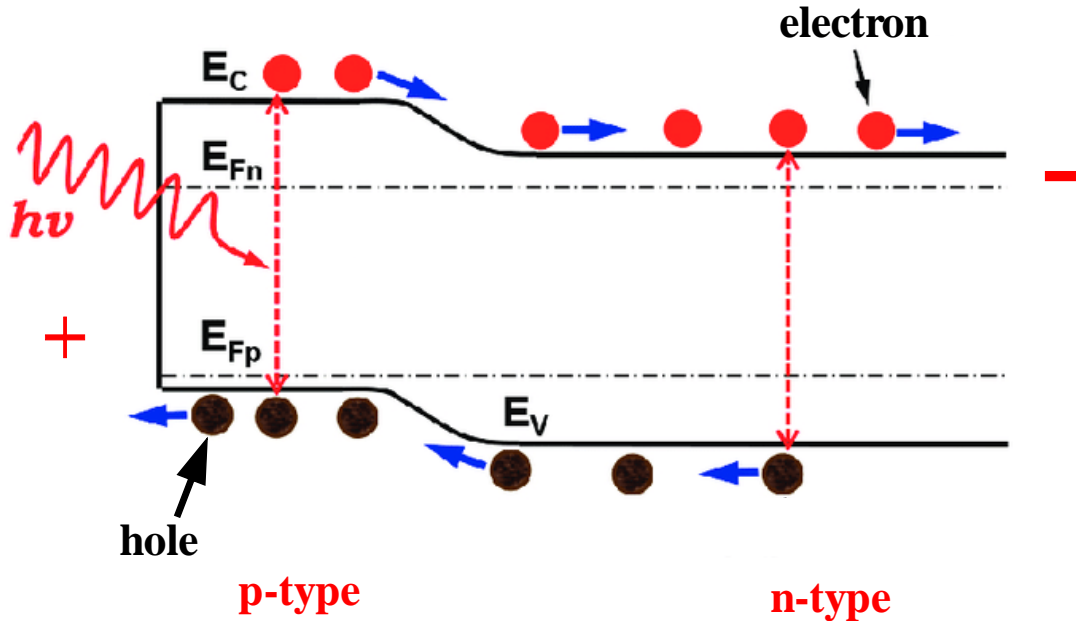


Figure 1.6: Band energy diagram of p-n junction solar cell under irradiation of light.[18]

1.3.1.1 First Generation Solar Cells

The silicon wafer is used to fabricate the first-generation solar cell. In 1954, American physicist Russell Ohl was the first introduced in Bell laboratories and achieved the efficiency around 6%. Due to high efficiency and durability these types of solar are more common in photovoltaic market. The first generation solar are made from only pure form of silicon. The silicon is most second abundant materials in Earth's crust but the availability of the pure form of the silicon is very rare. Generally, the availability of silicon in form of silicates (silicon dioxide). The purification of

silicon from its impure form is required a big amount of energy and due to which the cost of the photovoltaic solar cell is increases. There are two types of silicon based solar cells are available in PV market: (1) monocrystalline solar cells (2) polycrystalline solar cells.

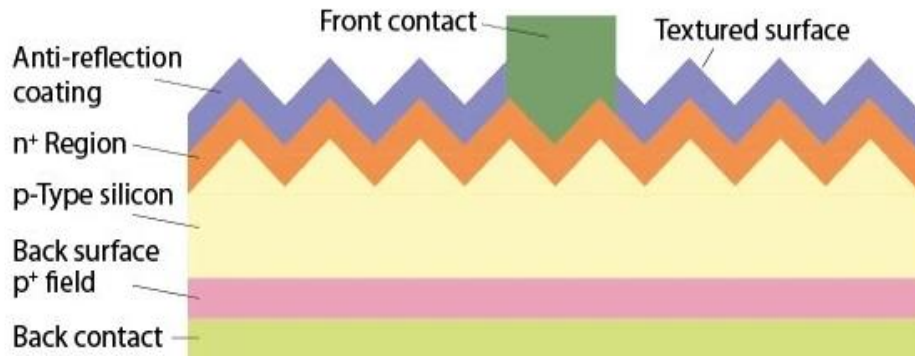


Figure 1.7: Cross-section of monocrystalline silicon solar cell.[19]

The Czochralski process[20,21] is used to obtain the high pure monocrystalline silicon wafers. The polycrystalline pure silicon wafers are prepared by using the various types of technology such as ingot and ribbon drawing.[22-24] The working principle of the first-generation solar cells is based on the principle of p-n junction. The top of the solar cell is n-region, light falls on this region hence, a highly doped thin layer is required for the better penetration of the light in this region. The p-region is thick and poorly doped. The cross-section image of the monocrystalline silicon solar cell is shown in Figure 1.7. The efficiency of the monocrystalline solar cells is higher than the value of the polycrystalline silicon solar cells. The highly efficient monocrystalline solar cells efficiency is 25 % is reported.[19]

1.3.1.2 Second Generation Solar Cells

The second-generation photovoltaic solar cell is based on the thin film technology. The high cost of the first generation of the solar cell is requirements for the development of the thin film technology, in these generation solar cell the very thin layer of the active materials is deposited on the supporting substrate. The requirements are, to reduce the quantity of the costly materials as well as to increases the flexible nature of the devices. The deposition of thin film on the substrate are takes place by using a various chemical (chemical vapor deposition) and physical method (thermal evaporation, sputtering process etc.) are available. The deposition of the thin films on the substrate is require a lower temperature as compared to the first-generation solar cells. The cell and module fabrication process are same but in case of the silicon-based technology the solar cell module made by integrating many cells in a series. The active materials properties such as conductivity, band gap, electron life time and diffusion length can be tuned to optimized the device performance. The transparent conducting oxide glass used as substrate and the metals and flexible plastics are employed to minimized the current loss in thin film cells due to substrate high sheet resistances.[25-27]

The thin film technology is classified in to four types on the basis of their structures:

- a) homo junction solar cells i.e. (p-n junction with same materials),
- b) hetero junction solar cells, i.e. (p-n junction with different materials),
- c) intrinsic amorphous silicon based solar cell, i.e. (p-i-n junction thin film), and
- d) multijunction thin film cells.[28-31]

The charge separation mechanism is same in thin film cells as traditional silicon wafer base solar cells. However, the amorphous silicon-based cells follow the working principle of p-i-n junction

solar cells. This is because of the fact the charge separation is depends upon the drift mechanism rather than diffusion mechanism due to the carriers having low lifetime and this is explained by using the band diagram of the p-i-n junction are shown in the Figure 1.7.

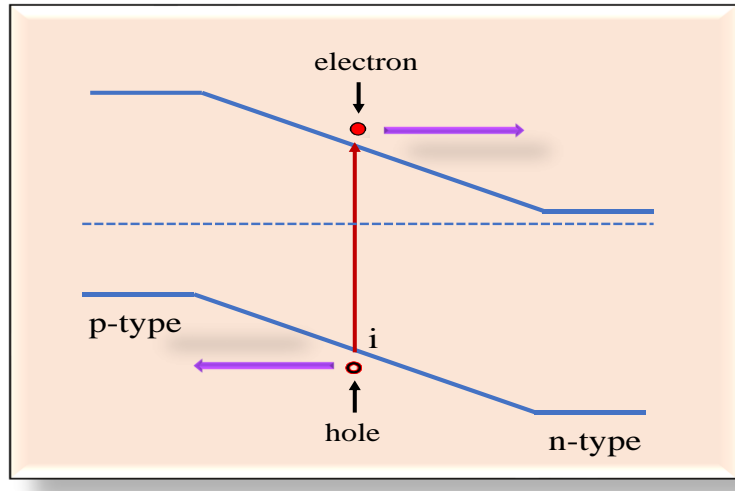


Figure 1.8: Energy band diagram of p-i-n junction under the irradiation of light.

When the p-i-n junction are irradiated under the sunlight then electron hole pair are generated in the intrinsic semiconductor region, the electron moves to n-region and hole drift to p-region is due to generation of the electric field in intrinsic amorphous silicon region. This electric field helps to separate photogenerated electron hole pairs with low lifetime.[32] The schematic diagram of thin films solar shown in the **Figure 1.9**. Thin films solar cells are fabricated by using the copper indium gallium selenide or copper indium gallium diselenide, cadmium telluride, cadmium sulfide and amorphous silicon as active materials in devices.[33-35] The CIGS thin film shows the high efficiency in laboratory around 20.3 % power conversion efficiency.[36]

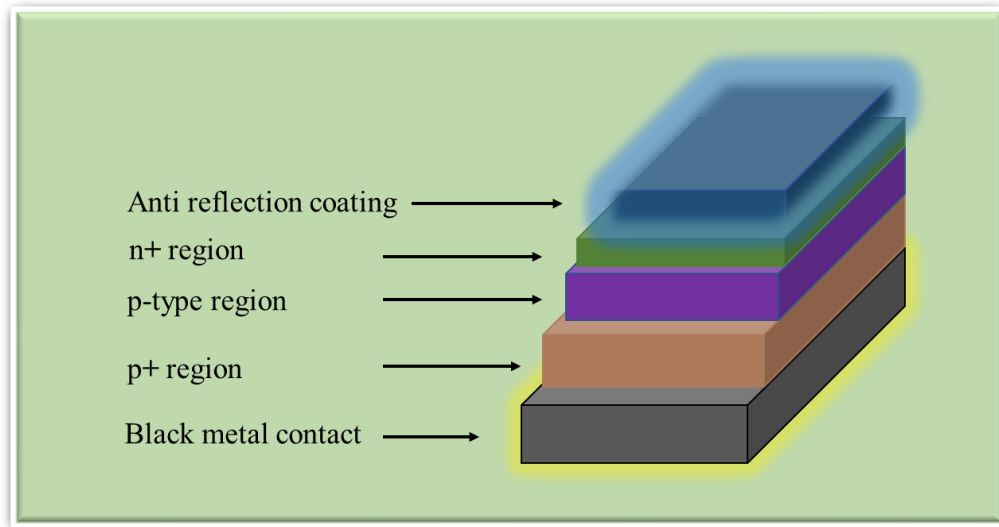


Figure 1.9: Schematic diagram of a thin film solar cell.

1.3.1.3 Third Generation Solar Cells

The term third generation solar cells are arising from the development of the previous solar cell's technology i.e., first generation base on silicon wafer and second-generation thin film solar cells.³⁷ To remove the shortcomings of the previous solar cell's technology, another technology was proposed known as third generation solar cells, firstly to improve the power conversion efficiency of the devices, secondly to reduces the production cost of the devices. The Shockley Quisser limit for a single junction solar cell is 33-34 % under AM1.5 illumination and in case of the multijunction solar cells using the various absorber layers to harvest the light from different regions of the solar spectrum to minimized the thermalization losses and achieved the high-power conversion efficiency i.e., more than 46 % efficiency.[37] The major problems of these types of

solar cells devices are the manufacturing cost and the third-generation solar cells technology are tried to reduce the manufacturing cost of the devices by using the low-cost processing techniques.

1.3.1.3.1 Organic Solar Cells

The organic photovoltaics solar cells also known as polymer solar which is fabricated by using the conducting organic polymer materials. The organic polymer absorption coefficient is high, tunable band gap and light weight nature of this devices are giving an advantage of such kinds of the solar cell as compared to the previous technology used to fabrication solar cells.[38-40] The organic photovoltaic solar cells are fabricated by using the carbon based light absorbing materials in devices and these types of the solar are belong from excitonic solar cells which are characterized by the presence of the bounded electron hole pairs under the illumination of the light.[41,42] The organic materials having low dielectric constants are used hence, due to which the electrostatics forces of attraction between electron hole pairs are relatively high. The generation of the free charge in organic system is behaves as barrier in the stability of the excitons, and it happened more effectively in other kinds of the solar cells. The dissociation of the exciton in organic solar cells is only takes places in interface region between the two types materials having different electron affinities i.e., an electron-donor materials.[30] The maximization of the area of this interface is an important consideration in the deposition of these materials. The bulk-heterojunction concept is suitable condition for such kind of the photovoltaics,[43] in this concept the donor and acceptor materials intermixing take places in separated phase resulting the more area are available for the interfaces which enhanced the generation of the free carriers in devices. The photo physics behind this system are highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the donor and acceptor materials which are conceptually more similar to

conduction and valence band of the inorganic semiconductor. The photo physics are further divided in four categories:[44]

- a) absorption of light and generation of exciton
- b) diffusion of excitons,
- c) generation of charge by dissociation of exciton, and
- d) transportation of charge and charge collection.

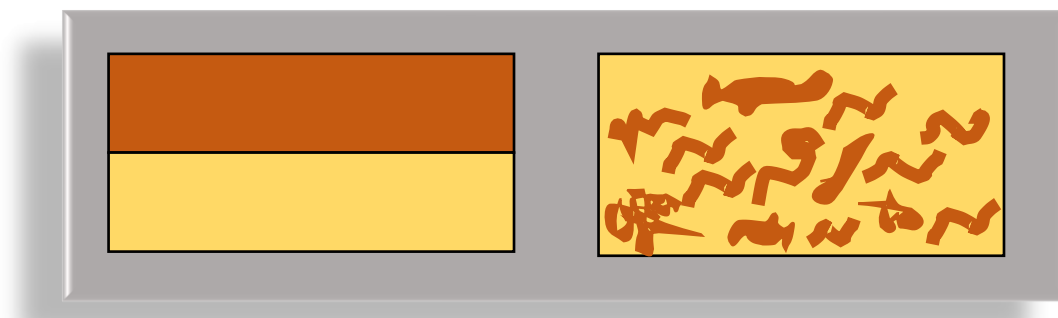
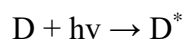


Figure 1.10: Differences between a bi layer junction (a) and a bulk heterojunction (b).

Absorption of Light

The active layer (donor materials) is absorbed the light in solar cells, and after the absorption of the light the electrons are get excited in LUMO level from the HOMO level resulting the formation of the excited state in the donor phase (D^*)



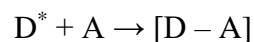
After the excitation of electrons, a vacancy was created in HOMO level; which is known as the hole and these are two charges are bonded by coulomb interaction and knowns as exciton.

Diffusion of Exciton

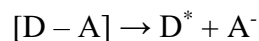
There are two types of the exciton i.e., one is Frenkel exciton and another is Wannier-Mott excitons. These two excitons are differentiated by the dielectric constants of the materials, which reflects how tight the electron and hole are bound. The Frenkel exciton having the low dielectric constants as compared to the Wannier exciton.[45,46] The Frenkel types exciton are generated in organic photovoltaics.

Generation of Charge by Dissociation of Exciton

The binding energy of an exciton is the energy necessary to separate the electron and the hole. The binding energy of Frenkel types exciton around 1 eV.[45] In order to be separated the exciton must travel along the donor phase until the interface with the acceptor phase. The acceptor materials having high electron affinity to separate the exciton in to the free-charges. At the interface the exciton forms a transition state defined as charge transfer state.[47]



And, if the charge state doesn't recombine it further evolves, separating into free charges, the positive hole in the donor phase and the negative electron in the acceptor phase (A^-)



Transportation of Charge and Collection

If the charge transports state is dissociating then two free charges are generated and the coulomb interaction is disappearing and these two charges are free to moves in their respective phases.

There are several mechanisms in this stage that can hamper the extraction of carriers, the free charge may recombine with other free carriers non geminately or they can thermalize into closed domain of a donor/ acceptor phase. The choice of which types of materials are mixed together in bulk heterojunction is based on energy levels of the two materials. For the efficient charge separation, it is necessary that there is a positive difference in energy between the HOMO and LUMO of the donor and LUMO energy level of the acceptor. The suitable band alignments are another important part of the internal field which is responsible for the charge separation and photovoltage of the solar cells.

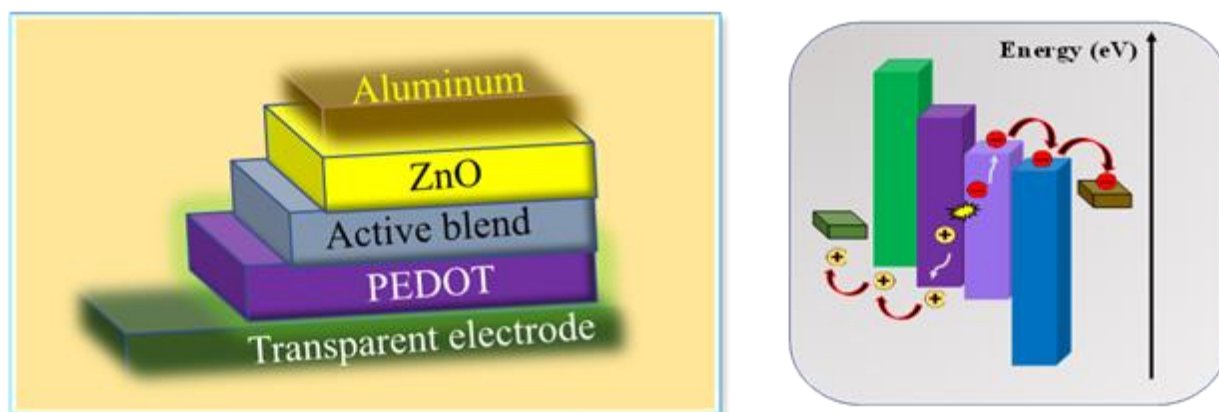


Figure 1.11: Structure and energy level for a standard BHJ solar cell. The active blend is composed by the intermixed phase of the donor and acceptor materials.

The most common donor materials used in BHJ solar cell is poly 3-hexylthiophene (P3HT) semiconductor polymer. This semiconductor polymer belongs to the thiophene polymers family. The P3HT polymer shows the good semiconductor properties as compared to other relatively simple synthesis. The BHJ solar cell shows the high efficiency around 5.5 % using the P3HT

polymer, and highest efficiency achieved by the any organic solar cell is around 11%. Some of the common materials are used in the BHJ photovoltaics solar cells are as a donor/acceptor include the P3HT/PEDOT: PSS, fluorinated benzothiadiazole and fluorinated fused subphthalocyanine dimer.[38-49] And the high work function electrode is used to fabricated the devices as compared to the low work function electrode is frequently previous technology.

1.3.1.3.2 Perovskite Solar Cells

In the recent year, perovskite solar cells have more attention for photovoltaics society, these solar cells also belong to the thin film technology. The structure of the perovskite solar cells is similar with the CaTiO_3 structure and the most common perovskite organometal halide are used in perovskite solar cells is $\text{CH}_3\text{NH}_3\text{PbX}_3$ (X can be a halogen element Cl, Br, I or a combination of them) and the structure are shown in Figure 1.12. The band gap rang for perovskite materials is 1.5 to 2.3 eV depending upon the halogens present in the perovskite crystal.[50-53]

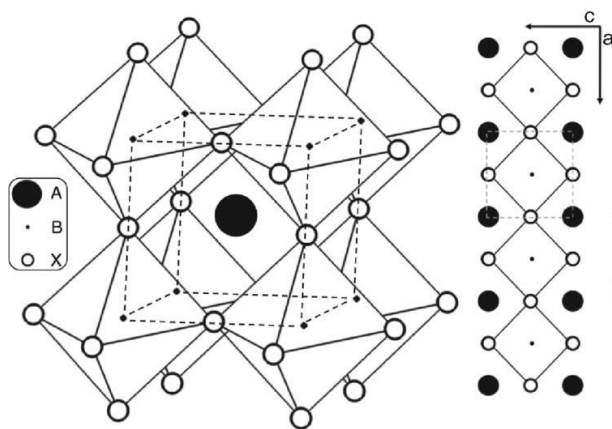


Figure 1.12: Perovskite structure of ABX_3 where $\text{A} = \text{CH}_3\text{NH}_3$, $\text{B} = \text{Pb}$, and $\text{X} = \text{Cl}, \text{Br}$ or I . [54]

The perovskite is used as light harvesting materials in solar cells and due to their panchromatic light absorption and ambipolar behavior, the performance of the solar cells is quite promising. The structure of the perovskite solar cells is similar to the DSC and a QDSC.

In 2009, the first perovskite solar cells were introduced by Tsutomu Miyasaka group with low power conversion efficiency around 3.8 %.[51] The perovskite materials are dissolved in electrolytes, due to which the durability of the cell is very less. Henry Snaith and Mike lee replaced the electrolyte by hole transport materials, they found that the durability of the cell was improved and perovskite materials itself transport the electrons.[54]

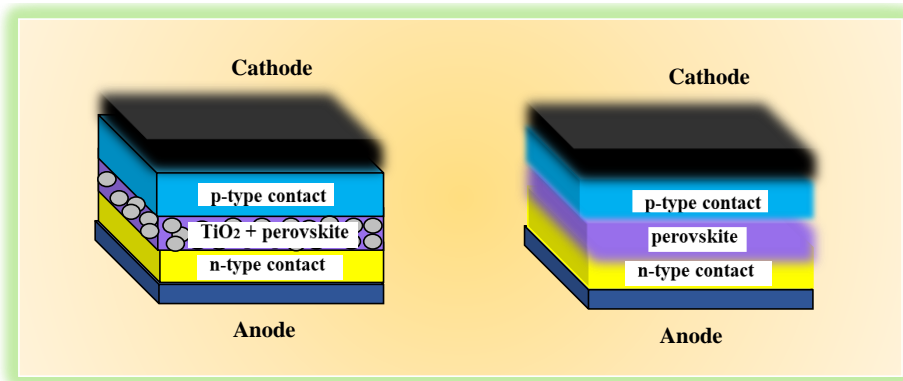


Figure 1.13: Two different types of perovskite solar cells diagram.

In 2016, Korea Research Institute of Chemical Technology (KRICT) and Ulsan national Institute of Science and Technology (UNIST) researcher in south Korea fabricated a single junction perovskite solar cell with achieved the highest certified power conversion efficiency 22.1 %.[55] The different types of the perovskite solar cell are shown in Figure 1.13.

1.3.1.3.3 Dye Sensitized Solar Cells

Dye sensitized solar cells are fabricating by using the Dyes as a light absorbing material, and due to easy fabrication process, low fabrication cost and high-power conversion efficiency as compared to the amorphous silicon based solar cells,[56-57] the DSSCs becomes more promising candidate for the next generation technology. In DSSCs, liquid electrolytes are frequently are used because it has the high electrical conductivity, easy fabrication process, low viscosity, and the good electrode-electrolytes interfacial properties, due to which the power conversion efficiency is high.[57] The power conversion efficiency for the DSSCs 11 % was achieved.[58] The open circuit voltage of the fabricated devices is depending upon the redox potential of the materials and chemical environments. The DSSCs with liquid electrolytes is suffer from the solvent vaporization, leakages, difficult to handle, and long-term stability and durability, these are the major problems was observed with liquid electrolytes in DSSCs, hence, the needs of the alternative technique to implants in solar cells technology which is free from the such kinds of problems. Thus, many research group was used the polymer gel electrolytes as a substituent of liquid electrolytes to fabricated the devices.[59] The polymer gel electrolytes have more attention in modern technology to improve the device performance. Ahn et al. was incorporated the polymer gel electrolytes in the DSSCs to obtained the power conversion efficiency around 7%. Dong et al. was prepared the polymer gel electrolytes by using the copolymer matrix, to replace the liquid electrolytes and achieved the power conversion efficiency around 8.84 %.[60] Tarrannum et. al. was also synthesized polysulfobetaine based gel electrolytes and fabricated the DSSCs and received the 6.82 % power conversion efficiency.[61] Wu et al. using the polyethylene oxide as conductive matrix to developed the polymer gel electrolytes for the DSSCs.[62] They observed that the photovoltage of the DSSCs is higher in case of the polymer gel electrolytes as compared

to the liquid electrolytes, hence the polymer gel electrolytes more promising candidates for the photovoltaics technology instead of the liquid electrolytes.

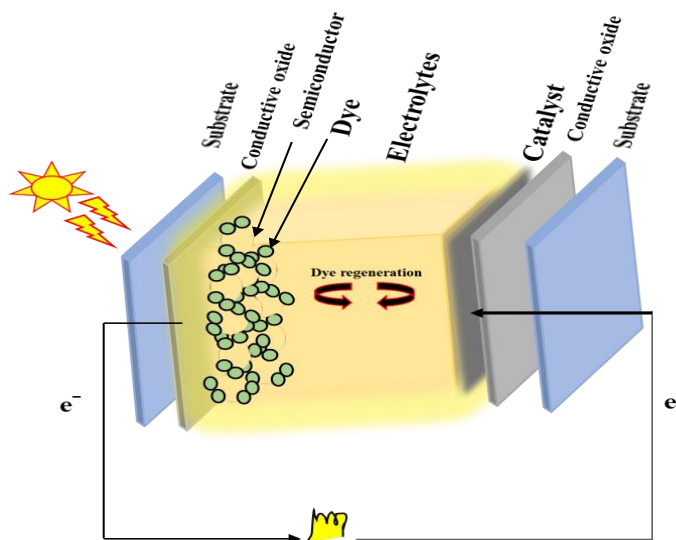


Figure 1.14: Structure diagram of dye sensitized solar cells.

1.3.1.3.4 Quantum Dots Sensitized Solar Cells

The QDSSCs have the same similar structure with DSSCs, in which dyes molecules are replaced by inorganic quantum dots semiconductors.[63,64] When the light is absorbed by organic dye molecules the devices are called DSSCs, whereas, the inorganic semiconductors are used as a light absorber / sensitizer, and size of the semiconductor is small enough to observe the quantum confinements effect such types of devices are called QDSSCs. The research works on the sensitization with wide band gap semiconductor such as dye molecules initiated since 1960s but in 1986,[65] Gerischer et. al., was first used the QDs for wide band semiconductor sensitization, and the improvement in research on sensitization lead to DSSCs. DSSCs and QDSSCs have many

similarities and some differences, and the major difference between these two is the sensitizer. The comparison between DSSCs and QDSSCs are shown in table 1.2.

Table 1.2: Comparison between QDSSCs and DSSCs.

S.N.	Component	QDSSCs	DSSCs
1.	Sensitizer	Sensitizer used is inorganic quantum dots such as, CdSe, Ds, Cited, etc.	Sensitizer include organic dye such as ruthenium based dye, etc.
2.	Wide band gap Semiconductor	A lot of work on QDSSCs utilized TiO ₂ as the one of photoanode components	A lot of work on DSSCs utilized TiO ₂ as one of the photoanode components
3.	Electrolyte	Works on QDSSCs, employs the polysulphide redox mediator in the electrolyte due to its stability towards quantum dots	Works on DSSCs employs the iodide based redox mediator in the electrolyte due to its stability towards DSSCs performance
4.	Counter electrode	Metal chalcogenides	Platinum

The advantages of QDs sensitizer are high absorption coefficient, ability of multiple exciton generation, tunable band gaps, low cost and photostability, which are reduces the dark current and increases the performance of the photovoltaics devices.[66] The main motivation of using the QDs as a sensitizer in solar cell is due to their tunable energy band gaps which control their absorption range. A monolayer of QDs nanoscale dimension is required as light absorbers / sensitizer in sensitized solar cells, hence, reduces the material requirement as compared to first- and second-generation solar cell which has micrometer thick absorbers. The sensitized solar cells work

efficiently both direct and diffuse light conditions and has been reported to have excellent recovery of the photocurrent after removal of heat stress. The major advantage for sensitized solar cells from their low fabrication cost and do not require a high energy consumption. The semiconductor TiO_2 are deposited on the FTO coated glass electrode for quantum dots loading. A number of the semiconductor quantum dots was synthesized (such as CdS, CdSe, PbS, PbSe, InP, and CuInS_2 etc.) by using chemical synthesis method and used as photoactive materials (light harvesting materials) to fabricated the photovoltaics devices. The optical band gap range values for the semiconductor quantum dots CdS, CdSe, and PbS are 2.2 – 2.42 eV, 1.78 - 2.25 eV and 0.34 - 0.37 eV respectively. The CdS and CdSe quantum dots harvest the light more effectively under UV radiation. The deposition of the quantum dots on photoanode take places by ex-situ and in-situ method. In the ex-situ method, firstly prepared the quantum dots and further deposition of quantum dots on photoanode by spin coating technique. And in-situ technique CBD and SILAR process are more common.

1.5 Device Structure and Working Principle of QDSSCs

The photovoltaic performance of any solar cells depends upon the three important factors:

1. The absorption of the solar light by the fabricated device. Hence, require high absorption coefficient materials for the device fabrication.
2. Under the irradiation of the light, the device must generate the significant number of charge carriers and the separation of generated charge carriers should occur properly in the device.
3. Appropriate collection of the charges must occur at the electrodes to receive the appreciable electric current output.

The structure of QDSSCs is constructed by considering three factors. A typical structure of QDSSCs consists of three main components:

- i. **a photoanode**
- ii. **a counter electrode**
- iii. **an electrolyte with redox couple.**

The QDSSCs are fabricated by inserted the electrolyte in between two electrodes using a spacer and sealed to prohibited the leakage of electrolyte. The device structure is shown in Figure 1.15. the inorganic semiconductor QDs in photoanode absorbs the solar light and produces the photoexcited electrons at the conduction band and simultaneously act as collector of charge carriers.

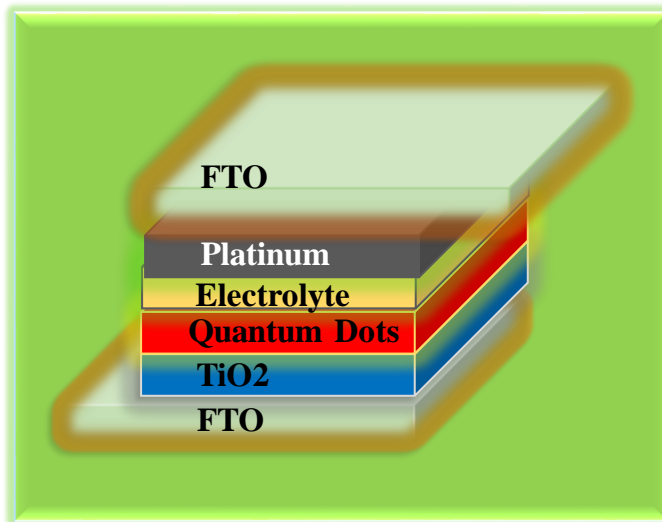


Figure 1.15: Typical device structure of QDSSCs.

The electrolyte provides an appropriate medium for the charge carriers (redox ions) transportation during the devices in operational mode. The photovoltaic performance and stability of the fabricated devices are also depending upon the properties of materials composition are used to prepared the electrolytes. The counter electrode reduces the oxidized charge carriers (oxidized ions of the redox couple) to complete the outer circuit. The all three components of solar cells are equally important and the performance of the QDSSCs is either directly or indirectly proportional to the all these three components.

1.5.1 Device's Components of QDSSCs.

1.4.1.1 Photoanode

In QDSSCs, the TiO_2 very frequently used as the wide band gap semiconductor with compared to the other oxides and cadmium chalcogenides (CdSe , CdS and CdTe) are most common out of several QDs chalcogenides for the preparation of photoanode. The important component for the photoanode in QDSSCs passivation layer. The passivation layer prohibited the electron recombination, which may increase the device performance and the short circuit current density will not be reduced. The fabrication process of cadmium chalcogenides is easy as compared to others which have tunable band gap and that can be controlling by their size. The optical band gap values are 2.3, 1.7, and 1.4 eV for CdS , CdSe , and CdTe chalcogenides respectively. Hence, the incident light in the visible wavelength can be absorbed up to 540 nm for CdS , 731 nm for CdSe and 887 nm for CdTe . A thin layer of TiO_2 paste was deposited on FTO coated glass substrate and further the QDs was deposited on the FTO/ TiO_2 layer to form the photoanode.

1.4.1.2 Counter Electrode

Another important element of a DSSC is the counter electrode. It does two main tasks:

- 1) It acts as a catalyst to decrease the oxidized ions (triiodide ions) by accepting electrons at the surface of the electrode. If the rate of decrease of the triiodide ions at the counter electrode is rapid, it enhances the electron flow from the counter electrode to the electrolyte phase. Consequently, higher electric current can be obtained at the outer circuit.
- 2) It fetches electrons from the external load and gives them back into circulation inside DSSC.

To fulfil these roles, the candidate for counter electrode must have the qualities listed below:

- Outstanding catalytic activity
- High electrical conductivity
- High surface area
- Chemical and electrochemical stability
- Corrosion resistance in the electrolyte environment, and
- Matching energy level with the potential of the redox couple in the electrolyte.

Platinum is the most suitable candidate for counter electrode because of its excellent catalytic activity. Various platinum-free catalysts have also been presented so as to decrease the use of the expensive platinum metal. These include carbon materials like graphene and carbon nanotubes, polymers like polyanilines and PEDOT: PSS, and many others.

1.4.1.2.1 Platinum

Platinum is the usually most chosen and counter electrode material for DSSCs. The photoconversion efficiency exceeding 12% have been attained using platinized counter electrodes.

The superior catalytic activity of platinum towards the reduction of triiodide ions, good conductivity for transport of electrons and its stability makes it predominant to other materials. Platinum is used in nanostructures form to enhance the surface area as well as the number of catalytic active sites.

Usually, a thin layer of platinum on a TCO glass substrate function as the counter electrode. Several techniques and starting materials can be used to produce platinum counter electrodes. Some of the accepted ones include thermal decomposition of chloroplatinic acid (H_2PtCl_6), H_2PtCl_6 reduction by hydrogen and electrochemical deposition, electron beam evaporation and sputtering of platinum. In 1997, Papageorgiou et al. modelled platinum counter electrodes on TCO substrates using both thermal deposition techniques (using H_2PtCl_6 at 380°C) and electro decomposition process.

Despite possessing several advantages, platinum also has a few drawbacks.

- It is very expensive. The cost of the counter electrode holds ~ 40% cost of the DSSC.
- It might undergo oxidation and/or dissolution forming platinum (IV) iodide (PtI_4) or iodoplatinic acid (H_2PtI_6) over time in the electrolyte environment containing iodide/ triiodide redox couple. Even a minute amount of Platinum, if dissolved in the electrolyte, can re-deposit on the TiO_2 photoanode and catalyze the reduction of triiodide ions, and short-circuit the entire device.
- There is energy mismatch between platinum and electrolytes containing redox couples other than iodide/ triiodide, such as cobalt- mediated electrolytes. So, it is not much effective in such surrounding.

These limitations have resulted in the exploration of platinum-free materials as worthy candidates for counter electrodes.

1.4.1.2.2 Graphene

Graphene is commonly used as a counter electrode material in DSSCs because of its better conductivity. The rate of charge transfer kinetics at the counter electrode is greatly enhanced due to its conductivity. The catalytic activity of graphene is increased in the presence of oxygen species or structural defects. These properties can be easily introduced during preparation of graphene. The accessibility of the raw material (graphite) and easy assembly method make graphene a very suitable aspirant for the platinum-free counter electrode material in DSSC. Also, the robust mechanical properties of graphene also facilitate flexibility to the electrodes. The pioneer work using Graphene as a counter electrode was studied by Xu et al. in 2008. A chemically reduced graphene oxide film as a counter electrode has shown 2.2% photoconversion efficiency. Over the years, the efficiency has upgraded appreciably. Zhang et al. attained photoconversion efficiency of 6.81% from the DSSC constructed with graphene nanosheets counter electrode. Studies have acclaimed that graphene-based catalyst surpassed platinum on using cobalt based redox electrolytes. Till now the efficiency with platinum counter electrodes has been limited to ~12%, while graphene counter electrodes have been found to furnish more than 13% efficiency. Mathew et al. used a layer of graphene nanoplatelets on fluorine doped tin oxide (FTO) coated glass as counter electrode and cobalt (II/ III) as a redox shuttle, which emerged in a DSSC with an efficiency of 13%. Kakiage et al. also resulted in obtaining the highest recorded efficiency of 14.3% by using graphene nanoplatelets on gold-treated FTO coated glass substrate as a counter and cobalt- mediated electrolyte.

1.4.1.3 Electrolytes

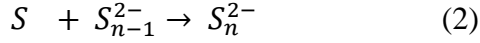
Electrolyte is the key components of a QDSSCs, electrolyte redox couple regenerates the QDs and transport the hole to counter electrode.[67] The efficiency of the device is estimated by its open circuit voltage, short circuit photocurrent density and the fill factor. The all three parameters will be significantly affected by electrolyte in QDSSCs, and by the interaction between electrolyte and electrode interfaces. The V_{oc} value is appreciably influenced by the redox potential of the electrolyte.[68,69] The J_{sc} is dependent on the transport ability of the electrolyte[70] and the fill factor value is affected by the catalyzing power of the counter electrode material to the redox couple.[71,72] Theoretically, the value of V_{oc} is dependent upon the energy difference between the fermi level of TiO_2 and the redox potential of the electrolyte. Depending upon their physical state the electrolytes are classified in three categories:

1. liquid electrolytes,
2. solid electrolytes, and
3. gel electrolytes.

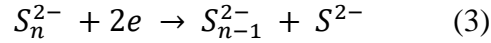
1.4.1.3.1 Liquid Electrolyte

Sodium sulphide and elemental sulfur were used to prepared the polysulfide redox couple in aqueous electrolyte as they can prevent QDs from degradation in electrolytes. The working mechanism of polysulfide electrolyte in QDSSCs can be explained by following process.⁷³ The holes are congregated by reduced species of redox couple at the photoanode and more precisely at the interface of photoanode/electrolyte (reaction 1&2).





After the ion diffusion process in polysulfide redox couple, oxidized species are converted back to S^{2-} by collecting the electrons at electrolyte / counter electrode interface (reaction 3).



The polysulfide redox couple is capable to mediate the charge carrier in QDSSCs efficiently, and most of the reported QDSSCs with higher efficiency used the polysulfide aqueous electrolyte. However, it was evidenced that the polysulfide electrolyte corrodes the cadmium chalcogenide photoanode. Recently, the Zhong's group was achieved the highest power conversion efficiency using the ZCISe QDs with a Cu/In molar ratio 0.7 under 1 sun illumination.[74,75] However other studies told that the aqueous polysulfide redox couple system is arduous to penetrate in to nano structural photoanode due to the high surface tension of the water and giving rise to inefficient contact between photoanode and electrolyte, resulting lower the device performance.[76-78] Hence, for the better penetration the lower surface tension solvents such as methanol may use to prepare the polysulfide electrolyte, but the ion dissociation capabilities of the methanol-based polysulfide electrolyte is lower than aqueous polysulfide electrolyte.[110-112] And, for the better penetration ability and higher ion dissociation capability, the water / methanol mixed solvent was proposed as a co-solvent to prepare the polysulfide electrolyte. Pan et. al.,[79] was fabricated the QDSSCs by using the water / methanol mixed as a co-solvent to prepare the polysulfide electrolyte and achieved the 5.32 % power conversion efficiency. Lio and coworker ware optimized the water / methanol ratio and to prepare the polysulfide electrolyte by using co-solvent and fabricated the QDSSCs device and they observed that the device performance was enhanced by 40 % due to good balance between penetration ability of solvent and ion dissociation in electrolyte.[78] The most

widely used electrolyte for QDSSCs is aqueous polysulfide redox couple due to its good compatibility with sensitizers and superior hole-extraction ability from the valence band of semiconductor sensitizers. The new redox couple systems such as I⁻/I₃⁻, Co²⁺/Co³⁺ complexes and some other redox couple have been tested in QDSSCs but failed to observed the higher power conversion efficiency due to the incompatibility of QDs with these electrolyte or charge recombination presented. Hence, for the higher PCE with polysulfide electrolyte needs to some modification. Ho et. al.,[80] were reported the CdS based QDSSCs by using the polysulfide electrolyte with the addition of the guanidine thiocyanate (GuSCN), and the PCE of the was enhanced from 1.79 % to 2.01 % by using the modified polysulfide electrolyte. Zhong's[81] group were obtained the 6.74 % PCE by using the polyethylene glycol as an additive in polysulfide electrolyte with CdSe based QDSSCs. A similar research works was reported by adding poly (vinyl pyrrolidone) (PVP) in polysulfide electrolyte.[82]

1.4.1.3.2 Solid State Electrolyte

The leakage and easy to vaporization of liquid electrolyte are major problem for the long-term stability of the photovoltaic devices with liquid electrolyte, in order to remove these problems, the many research group were introduced the solid-state hole transporting materials in photovoltaic devices. The solid-state hole transport materials have good thermal stability and easy to manufacture such as poly(3-hexylthiophene) (P3HT),[83-85] benzimidazolium (Ben),[86] 3,3'-didodecyl-quaterthiophene (QT12),[87] 2,2',7,7'-tetriks (N,N-dimethoxyphenyl amine)-9,9'-spirobiflourine (spiro-OMeTAD),[88-90] poly(3,4-ethylene-dioxythiophene) (PEDOT)[91] and inorganic p-type materials such as CuSCN[92] have been investigated to substitute the liquid electrolyte. Dang et. al., was reported the benzimidazolium salt based first solid-state electrolytes.

The 1,3-dihexylbenzimidazolium thiocyanate-based electrolyte with QDSC to achieved the 4.26 % PCE and 12.58 mA/cm² photocurrent density.[86] Chang et al prepared the solid state HTM spiro-OMeTAD based on Pb₅Sb₈S₁₇ nanoparticles for QDSC and achieved the 1.76 % PCE under 1 sun.[93] Zang et. al.,[94] fabricated the environment friendly QDSC by using the ZnO/Ag₂S core cell with P3HT conducting polymer and achieved the 0.363 % PCE. Therefore, the solid state QDSC have still shown much lower efficiency because of the mass transport limitation. Although the research on all solid state HTMs for QDSC application is in a primary stage, the promising peculiarly will trigger researcher to explore more efficient and stable QDSC materials and devices.

1.4.1.3.3 Gel Electrolyte

Generally, the liquid electrolytes are more common for QDSC. Despite the high conversion efficiency of photovoltaic devices, QDSC that employ a liquid electrolyte have the potential for other problems such as leakage, flammability, easily vaporize and performance instability. Thus, the use of the liquid electrolyte in conventional devices may also result in some practical limitations for the sealing and long-term stability. To improve the performance stability and sealing ability of the liquid junction QDSCs, an alternative solution gel state solar cells using the organic polymer and inorganic gelators was introduced.[60,95-102] The quasi solid state polymer electrolyte good thermal stability, high ionic conductivity, and better penetration ability in to nanocrystalline porous TiO₂ film, thus it has been widely used in QDSCs.[96,98,102,103] The liquid electrolyte is trapped in the network to form homogeneous quasi-solid-state electrolyte. There are many solid-state polymer electrolyte and gel polymer electrolyte are used to fabricated the QDSC. The performance of gel polymer electrolyte is better than the solid-state polymer electrolyte, because lower ionic conductivity and bad ionic transport ability. Yo and co-worker

used the hydrogel of the chemically cross-linked polyacrylamide-based polymer electrolyte to fabricate the QDSC with CdS/CdSe photoanode and obtained the 4.0 % PCE.[102] Zhong's group was reported the highest PCE 9.17 by using the quasi-solid-state electrolyte.[104]

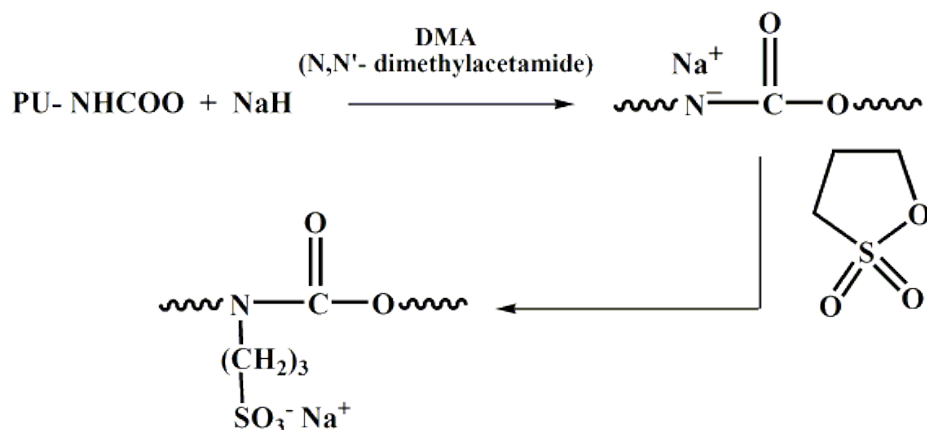
1.4.1.3.4 Polyelectrolyte

Polyelectrolytes consists of charged polymer having high ionic conductivity as well as good cohesive properties. Polymer ionomer containing some ionic group chemically attached with polymer matrix. Wen et al prepared the thermoplastic polyurethane-based polymer electrolytes and many research group prepared the PU ionomer with incorporation of the sulfonate, carboxylate and phosphate group in to polymer backbone and to enhanced the ionic conductivity of polyurethane polymer. Sulfonated copolymers are good candidate for the fuel cell membrane application. The important properties such as flexibility, swellability and dimensional stability of polyurethane ionomer may be controlled as per requirements. The most of the shortcoming of liquid electrolyte are replaced by using the polymer gel electrolyte in QDSC. The polymer gel state is stable at room temperature and it has good stability, higher ionic conductivity and long stability. Hence, due to these unique characteristics properties it become better alternative candidate to liquid electrolyte. Some research group ware used the non-ionic polymer as solidify agent with polysulfide electrolyte but such kind of the photovoltaic devices show the poor performance due to low ionic conductivity of the and diffusion of polysulfide electrolyte containing the non-ionic polymer. Hence, the polymer with high ionic conductivity is suitable candidate to solidify the polysulfide electrolyte. Feng et al prepared the polyelectrolyte by using the sodium polyacrylate ionic polymer with better water absorbing and water-holding capability to gelate the polysulfide electrolyte for QDSC. Therefore, it will be fascinating to adopt the polyurethane ionomer with the

ionized alkyl sulfonate moiety attached with polyurethane chain and it may be introduced in QDSCs.

1.4.1.3.5 Polyurethane Ionomer

Polyurethane ionomer includes the polyurethane polymer that have ionic sites, which have ions associated them. The polyurethane ionomer consists of polar group (1 to 15 mol % of ionic group attached with polymer chains) with urethane linkage and in which the charges are transported by ionic moiety of the polymer matrix, resulting the formation of the different kinds of nano and microstructure ionic clusters and ionic channels.



Scheme 1: Schematic reaction synthesis of the polyurethane ionomer.[105]

The ionic cluster is responsible for the conductivity and structural changes of the polymer. A variety of application were reported such as adhesive, coating, ink, automotive, textile, and the

most important application of the ionomer are in the fields of medicine and electronics technologies.[106] Recently, we have developed the thermoplastic polyurethane polymer gel electrolyte as a hole transports materials for quantum dots sensitized solar cells. The thermoplastic polyurethane polymers are chemically grafted by using the propane sultone and after the modification of polymer matrix with such pendent group the electrical conductivity is enhanced. The schematic representation of synthesis of polyurethane ionomer was shown in scheme 1. For the better devices performance required a high fill factor, open circuit voltage and low charge recombination rate by the incorporation of new redox active electrolyte for the devices.

1.5 Scope and Objectives of Present Work

Based on above research progress and analysis on electrolyte engineering it was observed that the chemical structure plays an important role for the establishment of the redox activity of the electrolyte's species. The major challenges behind the present work are high performance, low cost and easy fabrication techniques. Now a days, thermoplastic polyurethane polymer has more attention of the world scientific group due presence of multifunctional group on the soft and hard segment of the polymer matrix. Due to electrical insulating nature of the polyurethane polymer, the research and application have less attention in the field of the electrolyte, hence, the chemical tagging or covalent functionalization on urethane linkage of the polyurethane polymer may enhanced the electrical conductivity. Hence due to this chemical functionalization ability of urethane moiety of polyurethane, which have more attention of the world research group. The polar pendent group such as sulfonate, phosphate and carboxylic group was attached with polymer matrix which become the semiconductor in nature. It can be assumed that the ionically conducting

urethane linkage can suppress the photoexcited back electron transfer towards its electrolyte function without hindering the interfacial redox activity.

The main objective of this thesis is to develop and design the polymeric ionomer gel electrolyte through incorporation of the redox active pendent group at urethane linkage to generate the ionic conductivity. The ionic conductivity can be modified with variation of the chemical functionalization, nature and degree of pendent moiety, hard segment unit and nature of urethane linkage.

The main objective of the present work explores the following sub-objective.

- To understand the structure-property relationship of the polyurethane polymer with respect to redox active behavior and photovoltaic conversion efficiency.
- To enhanced the ionic conductivity of the polyurethane polymer by chemical attachment of graphene oxide and functionalized multiwalled carbon nanotubes on the polymer chain.
- To functionalized the urethane moiety and developed a polyurethane ionomer gel electrolyte as a hole transport material for the quantum dots sensitized solar cells.
- To understand the effect of additives (such as conducting carbon) on electrochemical properties (HOMO, and LUMO energy levels) and electrical conductivity of the ionomer gel electrolyte.
- To synthesized the suitable quantum dots (CdS, CdSe, CuInS₂) with various particle size and their optical band gap matched with ionomer gel electrolytes energy levels (HOMO and LUMO energy level) for fabricating the photovoltaic devices.
- To develop the photoanode on FTO coated glass by the deposition of various QDs and understand the effect of cosensitization on the photovoltaic device performance.

- To understand the effect of the temperature (annealing effect on photoanode) on the photoanode in terms of the photovoltaic conversion efficiency.
- To understand the effect of physical and chemical tagging of graphene oxide at polyurethane polymer and its gelation behavior.

1.6 Plan of the Present Work

To execute above objectives research work on the thermoplastic polymer gel electrolytes for quantum dots sensitized solar cell. The following plans of the work have been carried out systematically.

a. Functionalized thermoplastic polyurethane gel electrolytes for cosensitized TiO₂/CdS/CdSe photoanode solar cells with high efficiency.

- ❖ Synthesis of thermoplastic polyurethane by using aromatic diisocyanate, polyols (PTMG) and butanediol used a chain extender at constant 30 % hard segment content.
- ❖ Functionalization of urethane linkage of the thermoplastic polyurethane polymer by using the γ -propane sultone (various concentration) as sulfonating agents.
- ❖ Optimization of degree of functionalization of urethane linkage and found the suitable energy levels (HOMO and LUMO) of ionomer gel electrolytes.
- ❖ Analysis of the redox potential of the various degree of the functionalized polyurethane polymer.
- ❖ Estimation of the energy band gap of the functionalized polyurethane polymer with different extent of functionalization.

- ❖ Synthesis of CdS and CdSe QDs by using the solution mixing and hot injection method respectively.
- ❖ Analysis of cosensitization effect on the fabricated photovoltaic devices.
- ❖ Fabrication of the photoanode, counter electrode and fabrication of the quantum dots sensitized solar cells.

b. Functionalized polyurethane composites gel electrolyte with cosensitized photoanode for higher solar cell efficiency using a passivation layer.

- ❖ Synthesis of the GO-tagged polyurethane polymer by in-situ polymerization reaction.
- ❖ Functionalization of GO-tagged polyurethane polymer by using the propane sultone at two different chemical environments of the urethane moieties present on the GO-tagged polyurethane chain.
- ❖ Effect of the passivation layer on the photoanode $\text{TiO}_2/\text{CdS}/\text{CdSe}$ in terms of the photovoltaic performance.
- ❖ Measurements of the ionic conductivity of pure, go-tagged polyurethane and its subsequent functionalization.
- ❖ Calculation of energy band gap of the synthesized various quantum dots and functionalized polyurethane polymers with different extent functionalization.
- ❖ Analysis of the electrochemical properties.

c. Non-toxic CuInS_2 quantum dots sensitized solar cell with functionalized polyurethane gel electrolyte.

- ❖ Synthesis of f-MWCNTs-tagged polyurethane polymer
- ❖ Functionalization of f-MWCNT-tagged polyurethane polymer.
- ❖ Functionalization of MWCNTs.
- ❖ Electrochemical analysis of functionalized polyurethane polymer
- ❖ Measurements of electrical conductivity of the functionalized polyurethane polymer.
- ❖ Synthesis of the CuInS₂ quantum dots.
- ❖ Calculation of optical band gap of CuInS₂ quantum dots.
- ❖ Estimation of HOMO and LUMO energy levels of functionalized polyurethane ionomer and quantum dots.
- ❖ Measurement of inhibitor efficiency of the functionalized polyurethane ionomer.

d. The effect of chemical tagging of Graphene oxide in thermoplastic polyurethane on gelation behavior.

- ❖ Synthesis of chemically GO-tagged thermoplastic polyurethane polymer.
- ❖ Preparation of the gels by using the pure, physically and chemically GO-tagged thermoplastic polyurethane polymer.
- ❖ Determination of gelation rate of the various pure, physically, and chemically GO-tagged thermoplastic polyurethane polymer gel.
- ❖ Understand the effect of GO-tagging on polymer gel in terms of the viscosity flow behavior.
- ❖ Analysis of the rheological properties of the prepare various polymer gels.