Chapter 1

Photovoltaics: Basic concepts and developments

1.1 Introduction

Global power consumption of present civilized society is almost completely reliant upon non-renewable fossil fuels. Due to this, fossil fuels are depleting at a faster rate as the demand of energy is increasing day by day. Moreover, combustion of fossil fuels for energy production releases greenhouse gases that are responsible for disastrous effects on environment such as global warming and acid rain. We are in an irreversible, dangerous but avoidable circumstance that demands to replace the fossil fuel which hinders sustainable development of human civilization. While considering a suitable alternative to fossil fuels, it should be renewable, available in abundance, eco-friendly and capable of meeting growing energy demands. In this context, energy harvesting from sun is ultimate and perfect choice as it is ultra-clean, natural and sustainable source of energy. The energy supplied by sun on earth in one hour is equivalent to the amount of energy that is consumed by human beings in one year. Solar cells are the electrical device that directly converts sunlight into electricity based on photovoltaic (PV) effect. They have no moving parts and hence, after the initial installing cost, maintenance and repair costs are extremely low compared to existing technologies. Based on energy demand, they can be constructed to any size. For countries like India, the unused desert areas can be effectively used for installing solar cells. The concept of photovoltaic effect i.e., generation of electricity from light was discovered by Edmond Becquerel in 1839. At present, intensive researches are going on in this field. Now Si based solar cells are dominating this field with efficiency (at lab level) of 25.6 % [1]. But the higher cost for solar electricity, when comparing with existing technologies, still hinders the wide
spreading of this green technology. Thin film solar cells based on compound semiconductors are capable of overcoming the limitations of Si based technologies. Recent developments in this field are promising solutions for future energy demands.

1.2 Physics of solar cells

For most successful and versatile solar technologies, formation of a p-n junction using p-type and n-type semiconductors is essential. Nature and strength of internal built in electric field in a p-n junction is a critical factor in the operation of a solar cell. Light enters the solar cell through a window layer, which exhibits high electrical conductivity as well as transparency in the visible region of solar spectrum. Generally window layer is n-type material that ensures a low resistance contact to the device and transmits maximum amount of light to the absorber layer of the device. When light of suitable energy falls on the absorber layer of a solar cell, the electrons in the valence band get excited to the conduction band i.e., this results in excited electron in the conduction band and electron vacancy (hole) in the valence band. In effect, the electromagnetic energy in photon is now converted to the energy of electron-hole pairs. The built in electric field now comes into play and separates electrons to n side and holes to p side. If an external circuit is connected between this p and n-type region, the higher energy electron moves through this circuit. These electrons dissipate energy in the external circuit and finally return to the solar cell. For efficient solar cells, theoretically band gap of the light absorbing semiconductor material should be 1.4 to 1.6 eV [2]. Absorption coefficient of this absorber material should be very high to absorb maximum number of photons within a thin layer. Larger life time and diffusion length are preferable for minority carriers to enhance their better collection.

In practice, solar cells are connected in series to get the required voltage and in parallel to get required current. This arrangement of solar cells is
generally called a ‘photovoltaic module’ or ‘photovoltaic panel’. These modules/panels can be interconnected to form an ‘array’ for getting required electrical output.

1.3 Equivalent circuit of a solar cell

Solar cells are current sources. As long as the intensity of incident solar radiation is constant, current obtained from a solar cell remains same. The voltage obtained from a given solar cell depends on the external load connected and it varies with the load. Hence solar cell can be represented as a current source. If no external circuit is connected across a solar cell, the incident light will produce excess electrons at n side and holes at p side i.e., a potential difference will be created at the ends of the solar cell. This potential forward biases the junction and a diode forward bias current (I_d) flows through the diode. This diode forward bias current (I_d) is opposite to the photocurrent (I_ph) produced in the solar cell. Hence the net current (I) from a solar cell (Figure 1.1) is

\[ I = I_{ph} - I_d \]
\[ I = I_{ph} - I_o \left( \exp \left( \frac{-eV}{kT} \right) - 1 \right) \] .......... (1)

Where ‘I_o’ is diode saturation current, ‘e’ is charge of an electron (1.6 x 10^{-19} Coulombs), ‘V’ is the voltage between the terminals, ‘k’ is the Boltzmann constant and ‘T’ is the temperature in Kelvin.

If an external load (R_L) is connected to the solar cell, then I_d can still exist and the rest of the current will pass through the external circuit. When the light generated electrons travel through the solar cell materials and external contacts, they will experience a resistance. This resistance appears in series with the external load and is represented as ‘series resistance’ (R_s). For an
ideal solar cell $R_s$ should be zero so that there should be no voltage drop before the load. The equation for a solar cell in presence of series resistance is [3]

$$I = I_{ph} - I_o \exp \left[ \frac{e(V + IR_s)}{kT} \right] \ldots \ldots \ldots \ldots \ldots$$

The phenomenon of recombination of light generated carriers inside the solar cell material should also have to be considered. Due to recombination, these carriers cannot contribute electricity or it is shorted/shunted inside the device. A resistance corresponding to this process is represented as ‘shunt resistance’ ($R_{sh}$) in the circuit. For an ideal solar cell $R_{sh}$ should be ‘$\infty$’ so that there is no alternate path for current to flow and equation for a solar cell in presence of shunt resistance is given below [3].

$$I = I_{ph} - I_o \exp \left[ \frac{eV}{kT} \right] - \frac{V}{R_{sh}} \ldots \ldots \ldots$$

Series and shunt resistances of a solar cell are called its ‘parasitic resistances’. By dissipating power in these parasitic resistances efficiency of solar cells get reduced. Accurate determinations of these parasitic resistances have vital role in determining solar cell structure and hence its quality control.

The equivalent circuit of a solar cell is shown in Figure 1.1.

![Figure 1.1 Equivalent circuit of a solar cell.](image_url)
1.4 Output parameters of a solar cell

The main output parameters of a solar cell that are used to compare its performance with other solar cells are (1) Open circuit voltage ($V_{oc}$) (2) Short circuit current ($I_{sc}$) (3) Fill factor (FF) (4) Efficiency ($\eta$).

1.4.1 Open circuit voltage ($V_{oc}$)

Let us consider that no external load is connected to a solar cell or circuit is open. At this condition potential difference between the terminals of the device is maximum and the current through the external circuit is zero. The voltage across the output terminals of a solar cell in open circuit condition is termed as ‘open circuit voltage’ ($V_{oc}$). For an ideal solar cell ($R_{sh} = \infty$ and $R_s = 0$), equation for $V_{oc}$ can be expressed from eqn.1 as

$$V_{oc} = \frac{kT}{e} \ln \left( \frac{I_{ph}}{I_0} + 1 \right)$$

For higher $V_{oc}$ from a solar cell, the diode saturation current ($I_0$) should be as small as possible. $I_0$ decreases with increasing band gap of semiconductor material i.e., for higher value of $V_{oc}$, materials with higher band gap is required [2]. Bulk and surface recombination in semiconductor material are two fundamental factors that can limit $V_{oc}$ from a solar cell. Lower the recombination rate, higher the $V_{oc}$ [2].

1.4.2 Short circuit current ($I_{sc}$)

Let us consider that external load is removed and circuit is shorted. At this condition, voltage across the solar cell is zero and maximum current will flow through the circuit. The maximum current that can be obtained from a solar cell in short circuit condition is termed as ‘short circuit current’ ($I_{sc}$). From eqn.1, $I_{sc}$ for an ideal solar cell is

$$I_{sc} = I_{ph}$$
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$I_{sc}$ depends on area of solar cell. Hence while comparing the performance of solar cells with different areas; a term called short circuit current density ($J_{sc}$) is used. $J_{sc}$ is generally expressed as mA/cm² of the device. At a particular value of light intensity (generally 1000 W/m²), $I_{sc}$ from a solar cell depends on band gap and diffusion length of minority carrier in the semiconductor material. Lower band gap and higher diffusion length for minority carriers are preferred for higher $I_{sc}$. Optical losses such as reflective nature of semiconductor, reflection from metal grid contact on the side of the cell exposed to sun light and inefficient absorption of light with suitable energy due to the low absorber layer thickness can also reduce the $I_{sc}$ obtained from a solar cell [2].

1.4.3 Efficiency ($\eta$)

Solar cell efficiency is the ratio of output power obtained from a solar cell to the input power from the sun. The nature of general I-V characteristics of a solar cell is shown in Figure 1.2. At $V_{oc}$, voltage obtained from a solar cell is maximum, but current is zero, leading to zero output power at open circuit condition. At $J_{sc}$, current obtained is maximum but voltage is zero, leading to zero output power at short circuit condition also. Hence the maximum power point lies somewhere in the curve between $J_{sc}$ and $V_{oc}$. Theoretically the maximum power is selected in such a way that area of the rectangle created with this point as one corner in the I-V curve has maximum area. Let $P_m$ be the maximum power point with $V_m$ and $I_m$ corresponding to the voltage and current of the solar cell at that point (Figure 1.2). Then the maximum output power ($P_m$) from a solar cell is the product of this $V_m$ and $I_m$.

$$\text{Maximum output power } (P_m) = V_m \times I_m$$

$$\text{Efficiency } (\eta) = \frac{\text{Output power } (P_m)}{\text{Input power } (P_{in})} \times 100$$
\[ \eta = \frac{V_m \times I_m}{P_{in}} \times 100 \]

Standard test conditions (STC) for solar cell specifies a temperature of 25 °C and an irradiance of 1000 W/m² with air mass ratio equal to 1.5 (AM1.5). The Shockely Queisser limit calculations for solar cell efficiencies shows that only an efficiency of 34 % can be achieved for any type of single junction solar cells [4]. PV cells cannot respond efficiently to the entire spectrum of sunlight. As higher energy photons incident on the material, electrons are excited to higher levels in conduction band. These electrons quickly relax back to band edges and emit phonons. Thus a major portion of incident sunlight is wasted as heat. The photons with energy less than the band gap of the material are not absorbed, this process also wastes energy [2]. Recombination of electron-hole pairs can also waste a small portion of the incident energy depending on the semiconductor material. The efficiency limit of 34 % can be overcome by using multi junction solar cells.

Figure 1.2 I-V characteristics of a solar cell showing maximum power point.
1.4.4 Fill factor (FF)

Fill factor of a solar cell is defined as the ratio of maximum power \( P_m \) to the ideal power or theoretical power \( P_i \). Ideal power is the product of \( V_{oc} \) and \( I_{sc} \).

\[
\text{Fill factor} = \frac{P_m \cdot I_m}{V_{oc} \cdot I_{sc}} \times 100
\]

For an ideal solar cell, theoretical power and the maximum power are the same. Then the I-V curve will be a perfect rectangle with fill factor of 100 %. Practically I-V curves are not in perfect square shape and fill factor values ranges from 50 % to 82 %. Thus fill factor is a measure of ‘squareness’ of I-V characteristics of a solar cell.

![I-V curve of a solar cell for illustrating fill factor.](image)

Figure. 1.3 I-V curve of a solar cell for illustrating fill factor.

1.5 Solar cell materials and technologies

Current PV industry is dominated by silicon (Si) based solar cells. Monocrystalline and polycrystalline Si solar cells are well developed and their efficiencies have almost reached theoretical maximum values. Due to the unaffordable cost of Si wafers, thin film solar cells based on compound semiconductors are now gaining paramount importance. Most of the thin film solar cells contain earth abundant elements and can be easily deposited by simple, cost effective techniques. Organic photovoltaics also show promising
signs as future PV technology mainly because of their flexibility and simpler deposition techniques. The fields of polymer solar cells and dye sensitized solar cells are undergoing steady development. In order to overcome the Shockley – Queisser limit, active researches are going on in the above mentioned solar cell materials mainly by employing technologies like tandem solar cells, hot carrier solar cells, concentrated solar cells, up conversion, defect level assisted/intermediate band photovoltaics and quantum dot solar cells.

1.5.1 Silicon solar cells

Silicon solar cells can be divided into different categories according to the crystallinity or crystal size of the Si used for its fabrication. All Si solar cells work by the photovoltaic action of a p-n junction.

1.5.1.1 Crystalline silicon solar cells

Crystalline Si solar cells are highly efficient, oldest and still the most popular solar cells. Due to the energy intensive and sophisticated deposition techniques, their cost is not competitive with traditional means of electricity production. Czochralski method is used for growing Si wafers for fabricating crystalline solar cells. The wafers should have thicknesses ~ 200 µm for efficient light absorption as Si has indirect band gap. Boron and phosphorous are the dopants for making the wafer p-type and n-type. To improve the light absorption, wafer surfaces are generally textured. Another important issue is that these solar cells lose their efficiency as the temperature increases about 25 °C. Hence air circulation must be provided to these panels to maintain the efficiency. An efficiency of 25.6 % has been reported for n-type crystalline Si solar cells by Panasonic for a large area of 144 cm². A thin p-type amorphous Si layer served as the cell emitter and a similar n-type layer as the rear contact. It is a rear-junction cell having both positive and negative contacts in the unilluminated rear cell surface [1, 5].
1.5.1.2 Multicrystalline silicon solar cells

Wafers of multicrystalline Si are easy to prepare when comparing with monocrystalline Si. They are less efficient, but more cost effective than monocrystalline Si solar cells. Grain boundaries in multicrystalline Si are passivated by incorporating hydrogen during the device fabrication. Maximum efficiency of 20.4% was reported for multicrystalline Si solar cells [5, 6]. Ribbon Si is another type of polycrystalline Si formed by drawing flat thin films from molten Si. The process does not require sawing from ingots. Solar cells using ribbon technology possess lower efficiencies and are costlier than multi Si solar cells even though there is reduction in Si waste.

1.5.2 Thin film solar cells

Thin film solar cells using earth abundant elements are deposited by employing simple deposition techniques on comparing with Si photovoltaics. Hence both material and its processing are cost effective here. For solar cell fabrication only a smaller thickness of these materials are required due to their high absorption, small diffusion length and high recombination velocity. Hence very low weight per unit power is required here in comparison with crystalline Si technology. New concepts like tandem solar cell, hot carrier solar cells and multi junction concentrators are possible with thin film technology. A brief discussion about some important thin film solar cells are given below.

1.5.2.1 CdTe solar cells

CdTe is an ideal material for absorbing sunlight due to its direct band gap of 1.5 eV and high absorption coefficient. CdS was observed to be the suitable buffer layer for CdTe and CdTe/CdS is the only thin film solar cell so far to compete with crystalline Si in cost/watt. Major problem regarding this solar cell is the toxic nature of Cd and Te; again the limited supply of tellurium is another threat. Corrosion problem of the electrode was another major issue.
in CdTe solar cells. Also for the formation of good junction, an activation process in the presence of CdCl₂ is required. A variety of deposition techniques such as vacuum evaporation, closed space sublimation, chemical bath deposition and screen printing are available for CdTe deposition [7]. For device fabrication, usually chemical bath deposition and closed space sublimation are preferred. The best reported efficiency for CdTe based device is 19.6 % by GE global research [5, 8] and an efficiency of 17.5 % was reported by ‘First Solar’ (who are the pioneers in this material) for CdTe solar cell modules with an area of 7021 cm² [9].

1.5.2.2 Cu chalcogenides based solar cells

Copper indium selenide (CuInSe₂) thin films having a band gap of ~ 1 eV and higher absorption coefficient was observed to be suitable absorber layer. CuInSe₂ thin films are less sensitive to impurities and grain size, making it a better absorber layer. Due to low band gap, the open circuit voltage for CuInSe₂ based device was less than 0.5 V. Devices with an efficiency of 15.4% were reported for CuInSe₂ [14].

Copper indium gallium selenide (CuInGaSe₂ or CIGS) has the highest efficiency among chalcogenide thin films. Direct band gap of ~ 1.3 eV and high absorption coefficient make it highly suitable as an absorber layer in thin film solar cells. Presence of sodium (Na) in CIGS is very essential for grain growth and grain boundary passivation [10, 11]. A variety of techniques like co-evaporation and homogenization, vacuum deposition, sputter deposition followed by selenization, chemical spray deposition, screen printing and electroplating are available for CIGS deposition. Highest reported efficiency for CIGS solar cells in lab scale is 20.5 % by Solibro and an efficiency of 15.7 % was obtained by ‘Miasole’ in modular form with an area of 9703 cm² [12, 13, 5]. Multiple binary phases, structural and electronic disorders are possible in CIGS thin films; hence sophisticated control is required during the
deposition [7]. Also the limited supplies as well as high costs of indium and Ga are serious issues for CIGS based solar cells.

Copper indium sulphide (CuInS$_2$) thin films are important solar cell materials mainly because of their optimum band gap of 1.5 eV and high absorption coefficient of $10^5$ cm$^{-1}$, both are favorable for efficient light absorption. Moreover, it does not contain poisonous Se. A variety of deposition techniques like vacuum evaporation, sputtering, spray pyrolysis and atomic layer deposition can be successfully used for their deposition. CdS, In$_2$S$_3$, In$_3$(OH,S)$_y$, and ZnS are observed to be suitable buffer layers for CuInS$_2$ thin films. An efficiency of 12.5 % was reported for CuInS$_2$/CdS solar cell [15].

Cu$_2$S is another well studied absorber layer, mainly for Cu$_2$S/CdS solar cells. Cu$_2$S thin films are of particular interest because of their non-toxicity, earth abundance of constituents and simple production possibilities. An efficiency of 9.15 % was reported for Cu$_2$S/CdS solar cells way back in 1980’s [16]. But the diffusion of Cu from Cu$_2$S to CdS makes these solar cells unstable and Cd in the buffer layer is toxic. These factors hindered the developments of Cu$_2$S/CdS solar cells.

Materials like CuZnSnS$_4$ (CZTS), CuZnS and Cu$_2$SnS$_3$ are some of the recently developed semiconductor chalcogenide materials for solar cell applications. The constituents of these compounds are earth abundant and non-toxic. Moreover simple deposition techniques can be employed for their deposition. An efficiency of around 12 % was already obtained for CZTS based solar cells [17].

1.5.2.3 III-V solar cells

GaAs and InP are the important III-V compound for solar cell applications. These materials possess optical and electrical properties that are highly suitable for an absorber layer in thin film solar cells. Since high purity is
mandatory for these compounds in solar cells, sophisticated and costly techniques like liquid encapsulated Czochralski method, molecular beam epitaxy, liquid phase epitaxy, and chemical vapour deposition are used for deposition. These compounds are efficient but not cost effective when compared with other semiconductor materials used for thin film solar cells. Due to high power to mass ratio and radiation resistance, solar cells based on these compounds are excellent candidates for space applications. Highest efficiencies for GaAs and InP solar cells are 28.8 % and 22.1 % respectively [18, 19].

1.5.2.4 Amorphous silicon solar cells

Amorphous Si is the most well developed and widely accepted thin film technology to-date. Amorphous Si in thin film form possesses high absorption coefficient ($> 10^5 \text{cm}^{-1}$) and band gap of 1.5 eV. For efficient light absorption only few microns of this material is required, leading to low material cost for device fabrication. Amorphous Si is usually deposited employing ‘plasma enhanced chemical vapor deposition (PECVD)’of silane ($\text{SiH}_4$), over rigid as well as flexible substrates. Low temperature is required for deposition and by products of the techniques are environmentally benign. Due to the flexibility, amorphous Si is good choice for building integrated photovoltaics. Amorphous Si solar cells undergo degradation on exposure to strong sun light, these are not suitable for roof installation. This is mainly due to light induced breakage of Si-H bonds (Staebler-Wronski effect), leading to enhancement of density of dangling bonds which leads to a degradation in efficiency. An efficiency of 10.1 % is reported for amorphous Si (lab scale) [20].
1.5.2.5 Polymer solar cells

Polymer based solar cell technology offers light weight, mechanically flexible and eco-friendly solar cells through inexpensive fabrication techniques. A variety of simple technologies like roll to roll, spin coating, screen printing, doctor blading, inkjet printing and spray deposition can be used to deposit polymer thin films. As polymer deposition through these techniques are at low temperature, device fabrication over plastic substrates are also possible [21]. In polymer solar cell light absorption and subsequent exciton formation occurs in an active layer which consists of an electron donor and an electron acceptor. These excitons are seperated at the interface of donor and acceptor. The resulting electrons and holes are selectively transported to the metal contacts by selecting suitable electron or hole blocking layers. Generally used materials for polymer photovoltaics are P3HT, MDMO-PPV and PCPDTBT. Low efficiency (~ 10 %) and stability problems due to photochemical degradations are major draw backs of polymer solar cells.

1.5.2.6 Dye sensitized solar cells

In dye sensitized solar cells (DSSC), a dye is the photoactive material that absorb sunlight. Basic element of a DSSC is nanostructured material deposited over transparent conducting oxide (TCO). Nanostructured material usually consists of nanoparticles of TiO₂. Molecular sensitizers (dye molecules) then get attached to the semiconductor TiO₂ surface for absorbing sunlight. In the next step, a thin layer of iodide electrolyte is deposited over a separate conductive sheet (platinum metal). In the final stage of device fabrication, these two plates are joined and sealed together to prevent the electrolyte from leaking. Sunlight is absorbed by the dye layer and uses their energy to excite electrons, which is rapidly injected to the TiO₂ particles. The electrons flow towards the transparent electrode and later move through the external load. After that, they are re-introduced into the cell by a back metal electrode and
flows into the iodide electrolyte. The electrolyte then transports the electrons back to the dye molecules. In conventional solar cells, semiconductor assume both the task of light absorption and charge carrier transport. But in the case of DSSC, the two functions are separated. Light is absorbed by a dye molecule and the charge separation takes place at the interface between the dye and the semiconductor [22]. DSSC are semi-flexible, semi-transparent and simple to make using conventional roll-printing techniques. DSSC, which are the most efficient third generation solar cells, have major draw back of using of liquid electrolyte, which exhibits temperature stability problems. Moreover, the electrolyte is hazardous to human health and the environment. Higher cost of ruthenium dye, platinum catalyst and TCO still stands as major issues. An efficiency of 11.9 % was reported for DSSC (lab level) [23].

1.5.3 Tandem solar cells

Tandem solar cells are fabricated with multiple p-n junctions and each p-n junction responds to different energies in sunlight leading to an efficient absorption of sunlight. Here cells are deposited in the decreasing order of their band gap typically using metalorganic vapour phase epitaxy and the sunlight is illuminated from the sides of cell with higher band gap. Top junction absorbs the high energy photons. The lower-lying junctions then absorb consecutively lower photon energies. The individual junctions must be carefully connected via tunnel contacts [24]. In this way, the main energy loss mechanisms in single junction solar cells can be reduced. Maximum theoretical efficiency of 34 % for traditional single-junction solar cells can be overcome using this concept. Theoretically, infinite number of junctions would have limiting efficiency of 86.8 % under highly concentrated sunlight [25]. Tandem solar cells are now in commercial production (Natcore technology). An efficiency of 37.9 % was reported for InGaP/GaAs/InGaAs tandem solar cells [26]. Higher
‘price-to-performance’ ratio have limited their wide spread use. They are highly suitable for aerospace where high power-to-weight ratio is desirable. Concentrated photovoltaics (CPV) can be effectively used for these multi junction solar cells as it reduces cost/efficiency ratio. Here lenses and curved mirrors are used to focus sunlight onto multi-junction solar cells.

1.5.4 Hot carrier solar cells

Light generated carriers formed in conventional solar cells by absorbing photons of energy greater than the band gap lose their energy by cooling down from their initial energetic (“hot”) position to the band edges. Optical phonon emissions are also accompanied with this process. Hot carrier solar cells attempt to minimise this loss by extracting carriers at elevated energies in a narrow range. For extracting hot carriers, a substantial delay in carrier cooling in the hot carrier absorber and energy selective carrier extraction by an energy selective contact are essential [27]. At very high illumination intensities, significant reduction in cooling has been observed via a “phonon bottleneck” mechanism. This process has been demonstrated to be enhanced in quantum well (QW) nanostructures [28]. Recently, the concept of optical extraction was also developed for hot carrier cells. Optical extraction can be achieved with a layer consisting of silicon dioxide, Si nanocrystals and erbium ions (Er³⁺). The Si nanocrystals transfer its excess energy to the erbium ions, before it is lost as heat. This leads to the emission of several low-energy infrared photons per absorbed photon, which can produce extra electricity [29]. The limiting value of efficiency for hot carrier cell is 65 % at 1 sun and 85 % at maximum concentration - very close to the limits for infinite number of energy levels. But a more realistic limit of efficiency by considering some real material properties is closer to 50–55 % [30].
1.5.5 Multiple carrier generation in solar cells

In conventional solar cells, high energy photons create just one electron-hole pair, even though their energies are sufficient to produce two or more pairs. Evidence for the creation of more than one pair by high-energy photons is observed in bulk semiconductors like Si, Ge, PbS, PbSe, PbTe and InSb. This is attributed to impact ionization by the photo-excited carriers. Impact ionization in bulk semiconductors is not an efficient process. Threshold photon energy required for impact ionization is many multiples of the threshold absorption energy [31]. In the case of quantum dots, generation of multiple electron-hole pairs from single photon becomes very efficient. Threshold photon energy for this process to generate two electron-hole pairs per photon can approach values as low as twice the threshold energy for absorption [31]. In quantum dot solar cells, the excited electron-hole pairs remain as exciton and this process is called ‘multiple exciton generation’ (MEG). The performance of nanocrystal based solar cells can be improved using MEG.

1.5.6 Up and down conversion for solar cells

In conventional solar cells, the photons having energy less than the band gap of the absorber are simply transmitted. In up-conversion, two or more these low energy photons are converted into one high energy photon, which has sufficient energy to be absorbed. High energy photons in conventional solar cells lead to thermalisation losses. In down-conversion, these high energy photons, which are inefficiently absorbed by solar cell is converted into two or more lower energy photons. The photons thus generated have sufficient energy to be absorbed by the photovoltaic cell, with negligible thermalisation loss. A significant challenge for up-conversion is that it is a non-linear optical process and a very high intensity of incident light is required to produce only a small intensity of up-converted light. In the solar cell structure, up-conversion layer lies between the photovoltaic material and the back reflector. The down-conversion layer lies on top of the photovoltaic material. It is desirable
that the down-conversion layer must not interact with the light from the sun that is normally absorbed by the device [32]. For up or down conversion of light, nanostructures like quantum dots, luminescent dye molecules, and lanthanide-doped glasses can be employed. These nanostructures are capable of absorbing photons at a particular wavelength and emitting photons at a different (shorter or longer) wavelength [33].

1.5.7 Quantum dot solar cells

A quantum dot is a semiconductor nanostructure that confines the motion of its excitons in all three spatial dimensions. In quantum dot solar cell, quantum dots are the light absorbing photovoltaic material. Bandgap of quantum dots are tunable across a wide range of energy levels by changing size of the dots. Both, expensive molecular beam epitaxy and cost effective wet chemistry processing techniques can be employed for quantum dot preparation. An efficiency of 8.55 % (9.2 % in lab scale) was reported for ZnO/PbS quantum dot solar cells. The performance of this device remains same even after more than 150 days storage in air [34].

1.5.8 Plasmonic solar cells

In plasmonic solar cells, metal nanoparticles are used to improve the light absorption. Generally metal nanoparticles are deposited on the top surface of the thin film solar cell. When light incident on plasmonic solar cells, due to plasmon resonance of metal nanoparticles at the surface, the light is scattered in many different directions. This allows light to travel along the solar cell and bounce between the substrate and the nanoparticles. These processes enabling the plasmonic solar cell to absorb more light [35]. Ag and Au nanoparticles are generally used for plasmonic solar cells.
1.5.9 Intermediate band photovoltaics

In this type of solar cells, an intermediate band (IB) energy level is purposefully introduced in between the valence and conduction bands. Theoretically, due to the presence of this IB, two photons with energy less than the bandgap can excite an electron from the valence band to the conduction band. This enhances the induced photocurrent and thereby efficiency of the device [36, 37]. These are theoretically highly efficient devices but they are hard to make. Intermediate bands are possible in single junction devices by introducing small, homogenous quantum dots in it. By changing the size and shape of quantum dot, the intermediate band can be tuned [38]. Chemical spray pyrolysis (CSP) method can be effectively used for the creation of defect bands and mixed phases (there by double band gap) of absorber material in thin film solar cells. Chapters 4 and 5 deal with the experimental and device fabrication using this idea.

1.6 Chemical spray pyrolysis for thin film deposition

Based on the nature of the deposition process, thin-film deposition methods can be divided into two group viz., physical or chemical. Physical deposition employs mechanical, electromechanical or thermodynamic means to produce a thin film of solid. Physical vapor deposition (PVD), molecular beam epitaxy (MBE), laser ablation and sputtering are the major physical deposition methods. In chemical methods of thin film deposition, fluid precursor undergoes a chemical change at a solid surface, leaving a solid layer. Chemical methods can be divided in to two i.e., gas-phase deposition methods and solution techniques. Important gas-phase deposition methods are chemical vapor deposition (CVD) and atomic layer epitaxy (ALE). In sol-gel, CSP, spin and dip-coating methods, precursor solutions are employed for thin film deposition [39]. Simplicity and inexpensiveness are the main advantages of solution based chemical techniques and they have been studied extensively for
the preparation of varieties of thin films. Another important aspect of solution based techniques is that they facilitate materials to be designed on a molecular level [40]. Among different chemical methods, CSP proved to be a suitable method for the deposition of large-area metal oxide, mixed oxides, spinel oxide, binary and ternary chalcogenides and super conducting compounds [41]. The process is already widely applied and is attractive for the deposition of low-cost thin film solar cells, sensor applications, anodes for lithium-ion batteries and optoelectronic devices [42]. In spray pyrolysis technique, a precursor solution containing soluble salts of the desired compound is sprayed using an atomizer on to preheated substrate. On reaching the hot substrate the droplets of precursor solution under goes a pyrolytic (endothermic) decomposition and the constituents react to form a chemical compound. The precursor solutions are prepared such that the products other than the desired compound are volatile at the temperature of deposition. The volatile by-products and solvents escape in the vapor phase. Typical spray pyrolysis equipment consists of an atomizer, atomizer control mechanism, precursor solution and its dispensing mechanism, substrate heater and temperature controller.

CSP offers many advantages over other thin film deposition techniques.

1) CSP represents a very simple, versatile, vacuum free, industrially viable, cost-effective (especially with regard to equipment costs) technique which is extremely easy technique for preparing dense and porous films of any composition on any area.

2) Deposition rate and hence the thickness of the films can be controlled easily over a wide range therefore eliminating the main drawbacks of chemical methods like sol-gel technique that produces films of restricted thickness. Even multilayered films can be easily prepared using this versatile technique.
3) Doping is extremely easy in CSP; it can be done just by adding the required proportion of dopant in the precursor solution. By changing composition of the spray solution during the spray process, even thin films having composition gradients throughout the thickness can be deposited.

4) A variety of substrates in any dimension and surface profile can be utilized in CSP as it operates at moderate temperatures (100 - 500 °C).

5) Solvent can be simple like water or alcohol which are very eco-friendly.

6) CSP does not require high-quality substrates or chemicals. Variety of chemicals can be used for a particular thin film deposition.

7) CSP is suited for large area deposition which offers industrial production of cost effective thin film solar cells.

1.6.1 Different steps involved in CSP

Various steps involved in spray pyrolysis are atomization of the precursor solution, aerosol transportation to the substrate and decomposition of the precursor (most probably on surface of substrate) to initiate film growth. Each step is very crucial in CSP and the properties of the deposited films can be easily tailored by optimizing various factors involved in each steps.

1.6.1.1 Atomization of precursor solution

Atomization is the first step in spray pyrolysis that involves the formation of fine droplets of precursor solution and send them, with some initial velocity, towards the substrate surface. CSP generally uses air blast,
ultrasonic and electrostatic techniques for atomization. In air blast type atomizer, fluid emerging from a nozzle at low speed is made to ‘meet’ a high speed stream of air (carrier gas). Friction between the liquid and air accelerates and disrupts the fluid stream leading to atomization. Here pressure of carrier gas is the energy source of atomization [43]. For ultrasonic atomization, the precursor solutions are vapourized with an ultrasonic nebulizer which is operated at a particular frequency (generally 2.56 MHz). The vapor generated is transported by the carrier gas through a pipe to the heated substrate [40]. In electrostatic atomization, precursor solution is exposed to a high electric field, which causes the atomization. Droplet size distribution, rate of atomization and initial velocity of the droplets are different for each type of atomizers. It is very important to understand basic atomization process of the device used. Selection of atomizer depends on the application of thin films to be prepared, liquid properties and operating conditions [39].

1.6.1.2 Aerosol transportation

The aerosol formed after the atomization is transported to the hot substrate. During this transportation there are four forces simultaneously acting on it, describing its path. The forces are gravitational, electrical, thermophoretic and the Stokes force. Gravitational force on a droplet depends on its mass and pulls the droplet downwards. Here the droplet transport is driven by the gravitational force and the initial velocity. This process does not have contribution from an electrical force. For ultrasonic and electrostatic atomizer, electrical force is the main component which drives the droplets downwards. Generally, the electrical force acting on a droplet is several orders of magnitude larger than the gravitational force. When the droplet travels through the air, Stokes force comes into play as the droplet experience a drag due to air resistance. As Stokes force is proportional to the
droplets velocity and size, large droplets which move with high velocity will experience the largest retarding force [42].

As the droplets of precursor solution move towards the hot substrate, thermophoretic force comes into play. Gas molecules from the hotter side of the droplet rebound with higher kinetic energy than those from the cooler side. Thus thermophoretic force pushes the droplets away from a hot surface [39]. Studies showed that thermophoretic force has no effect on the droplet movement when it is more than several (~ 5-7) mm away from the hot substrate. However, below this limit, thermophoretic force begins to dominate due to high thermal gradient. In pressure spray deposition systems gravitational force is the main driving force. As a result, thermophoretic force has significant influence here. But in electric spray deposition systems, electric force is often stronger than thermophoretic force [42].

During transportation towards the hot substrate, droplets experience evaporation of the solvent and a concentration gradient is developed within the droplet. When the surface concentration of the droplets exceeds the solubility limit, the precursor precipitates on the surface of the droplet. Rapid solvent evaporation and slow solute diffusion leads to this precipitation. As a result of these processes, droplets are converted to a porous crust and subsequently hollow particles, which are not desired because they increase the film roughness. In CSP, it is desired that most droplets fly to the substrate without forming particles [39].

1.6.1.3 Precursor decomposition

In CSP, the decomposition of precursor depends on the substrate temperature. At lowest substrate temperature, the droplet from atomizer splashes onto the substrate and decomposes. This process leads to rough or
non-adherent films. At higher temperatures, the solvent evaporates completely from the droplets during its flight from atomizer to the substrate. Finally dry precipitate hits the substrate and decomposition occurs. At even higher temperatures, this solid precipitate melts and vaporizes without decomposition and the vapor diffuses to the substrate to undergo a chemical vapor deposition (CVD) process [39]. It involves the diffusion of reactant molecule to the substrate surface and its adsorption, surface diffusion and a chemical reaction, incorporating the reactant into the lattice, desorption and diffusion of the product molecules from the surface [42]. This CVD-like deposition is desired to yield dense, high quality films but it rarely occur in most spray pyrolysis depositions. This is because either the deposition temperature is too low for the vaporization of a precursor or the precursor salt decomposes without melting and vaporization. At the highest temperatures, the precursor vaporizes before it reaches the substrate, and solid particles are deposited on the substrate as result of the chemical reaction in the vapor phase [39]. This process also leads to rough or non-adherent films.

### 1.7 Factors affecting CSP

Important factors that can affect nature of thin films deposited by CSP are composition of precursor solution, substrate temperature, spray rate of the precursor solution, deposition time, nozzle to substrate distance and pressure of carrier gas.

**Composition of precursor solution:** For spray pyrolysis, precursor solution is generally prepared by dissolving inexpensive metal salts like metal nitrate, chloride, acetate or sulfate in solvents like water or alcohol. Physical and chemical properties of the precursor solution have strong dependence on solvent, type of salt, concentration of salt and additives [39]. Nature of solvent
used in precursor solution determines its boiling point, solubility of salts and spreading behavior of droplets on the substrate. The salt must be easily available, non-toxic and should possess high solubility, which increases the yield of the process. Because of the possible by-reactions such as hydrolysis, polycondensation, etc. between the precursors, special care is required in handling the precursor solution. These by-reactions leading to solubility problems and phase segregation and the different components precipitate close to the working conditions [44].

**Substrate temperature:** Substrate surface temperature is the most important parameter in CSP that determines film morphology, electrical and optical properties. Except aerosol generation, deposition temperature plays vital role in all other thin film deposition steps in CSP. The properties of deposited films can be effectively manipulated by changing the deposition temperature. As substrate temperature increases, the film morphology can change from a cracked to a porous microstructure [39].

**Spray rate:** As spray rate increases, quantity of solution hitting the substrate surface in unit time increases which decreases the substrate temperature from a pre-set value. Since the drastic variation in spray rate affects the substrate temperature, spray rate can be a critical parameter in CSP. It was observed that by spraying same volume of precursor solution at different spray rates, thicknesses of the deposited films are increasing by increasing the spray rate. This may be due to re-evaporation in presence of higher temperature at lower spray rate.

**Deposition time:** In CSP, as deposition time increases, thickness of the deposited films increases. Thin films of many materials get peeled off as deposition time increases beyond a limit.
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Nozzle to substrate distance: The sprayed droplets come out of the nozzle at a particular spraying angle. As substrate–nozzle distance decreases, the coverage of spray over the substrate decreases. Smaller is the distance of atomizer to the substrate higher the deposition rate. This also makes the coated area smaller.

Pressure of carrier gas: In pressure spray deposition systems, pressure of carrier gas can manipulate the droplet size of the sprayed precursor solution. Generally as the pressure of carrier gas increases, droplet size decreases.

### 1.8 CSP deposition for the present study

An automated chemical spray pyrolysis machine was employed for thin film deposition in this study (Figure 1.4) [45]. The essential parts of this unit are

a) Atomizer and its controlling mechanism – An air blast type atomization was made possible using a surgical needle and ordinary compressed air. The atomizer is connected to a microprocessor so that it is made to move over the entire substrate surface to get uniform coverage over the substrate.

b) Substrate heater – The required temperature for the substrate is provided by a heater using which temperature can be varied from room temperature to 773 K. The heater can provide uniform temperature over an area of ~ 50 cm² and the temperature is measured using a K-type thermocouple attached with the heater. Temperature controller with feedback circuit was used for providing constant substrate temperature during the spray.

c) Solution dispenser – A container, made up of teflon, having motor controlled piston was used for dispensing precursor solution in to the
atomizer. The rotation of motor and hence the spray rate is controlled by the microprocessor.

d) Air compressor and gas controller – Atmospheric air was compressed using an air compressor (1HP, storage capacity = 45 litre). The pressure of air from the compressor to the atomizer is controlled and measured by a mechanical gauge.

Figure. 1.4 Photograph of the automated CSP machine for the present study.

1.9 Review on CuInS$_2$ and Cu$_2$S thin films

1.9.1 Deposition of CuInS$_2$ thin films

A variety of physical and chemical methods are available for the deposition of CuInS$_2$ thin films. Evaporation techniques are the most common deposition techniques for CuInS$_2$ thin films which yield good quality films. Scheer et al. reported deposition of CuInS$_2$ by co-evaporation on borosilicate glass substrate. Surface composition of the films is investigated by employing X-ray and ultraviolet photoelectron spectroscopy. A comparison of the front
and back surface, i.e., the interface between the Cu–In–S film and the Mo back contact, is done for films with different stoichiometry. Indium-rich films are covered at both surfaces by an indium-rich second phase, viz., CuIn$_2$S$_2$. The front surface of Cu-rich films shows aggregation of CuS and it was not found at the back surface [46]. The in-situ doping of N, P, Sn as well as the impact of these elements on electrical properties of co-evaporated CuInS$_2$ thin films was studied. On doping with Sn, n-type conductivity was not observed in CuInS$_2$. Phosphorous incorporation was possible only in the presence of Sn atoms (co-doping). Also Na, P co-doping leads to a decrease in conductivity of CuInS$_2$ films. It was observed that conductivity of the films decrease with increasing nitrogen concentration [47].

Two source evaporation (Cu and In) followed by a three source evaporation (Cu, In, and NaF) produced Na doped Cu-In precursor films having different Na concentrations. Sulfurization was performed immediately at the same evaporation chamber to form CIS thin films. The (112) preferred orientation in CuInS$_2$ was enhanced by the addition of Na but the grain sizes of the CIS films decreased with Na doping. It was observed that Na is distributed homogeneously in the deposited films. Also resistivity of the films decreased with Na doping. The phase transformation from CuInS$_2$–CuAu structure to CuInS$_2$–chalcopyrite structure was not altered during sulfurization even though Na is incorporated in the films [48]. Photoelectron spectroscopy studies on evaporated CuInS$_2$ shows that the Fermi level position is varying from $E_F - E_v = 1.3$ eV for In-rich to $E_F - E_v = 0.0$ eV for the Cu-rich films [49]. The surfaces of evaporated CuInS$_2$ films were also investigated with the help of X-ray photoelectron spectroscopy (XPS). Surface properties of CuInS$_2$ films are highly sensitive to alterations in the bulk stoichiometry. For slightly indium rich films an enrichment of indium and depletion of Cu occur at the surface. Surface composition of these films corresponds to the stoichiometry of
CuIn₃S₅. Cu-rich films exhibit segregation of a CuS phase as indicated by an additional Cu-Auger structure in XPS analysis [50].

Hwang et al. reported deposition of single phase CuInS₂ thin films employing flash evaporation. Deposited films are analyzed using X-ray diffraction and atomic absorption studies. Source temperature was found to be the dominant factor for the formation of single phase CuInS₂ thin films. Flash deposition conditions are derived and they concluded that it would be very difficult to prepare single phase CuInS₂ thin films through flash evaporation [51]. Agarwal et al. reported the formation of single phase, n-type CuInS₂ thin films of thickness between 60 nm and 650 nm with the chalcopyrite structure on NaCl and glass substrates by flash evaporation. Influence of substrate temperature on the properties of the films were investigated and it was observed that molybdenum source temperature of 1873 K and a substrate temperature of 523 K were the upper limits for obtaining reproducible results and single phase n-type CuInS₂ thin films [52].

Abaab et al. reported the deposition of CuInS₂ thin films (single source vacuum thermal evaporation method) on substrates submitted to longitudinal thermal gradient. Cu, In and S elements having 99.999 % purity were used to prepare the initial ingot of CuInS₂. Some of these films were sulfurized to obtain homogenous CuInS₂ thin films. As-deposited and sulfurized films were characterized using X-ray diffraction, optical transmission and reflection measurements. As deposited CuInS₂ films deposited contain Cu₇In₄ and In aggregates. On annealing in S atmosphere, these secondary phases were converted into CuInS₂. After annealing in S atmosphere, film surfaces are covered by a segregated CuₓS (x = 1.96 and 2) phase and optical band gap of these films were 1.50 eV which is the optimum value for photovoltaic energy conversion [53]. Glancing angle deposition (GLAD) was used for depositing
CuInS$_2$ films with highly orientated microstructure composed of slanted columns. In absence of the substrate rotation, as the incident angle was increased, nanocolumns are progressively inclined towards the evaporation source. When the substrate is rotated at an angle of 80 ° during film deposition, the nanocolumns become wire forms only for elevated rotational speeds. It was observed that island formation in the film was enhanced due to shadowing effect, introduces preferential growth on taller surface heights [54]. Rabeh et al. investigated the effect of post-growth treatments in air atmosphere on structural, morphological, optical and electrical properties of CuInS$_2$ thin films prepared employing vacuum thermal evaporation on non-heated glass substrates. It was observed that on annealing at temperature above 200 °C, the n-type conductivity is stable. The band gaps of the samples after annealing are in the range of 1.45–1.50 eV [55].

The effect of bismuth doping in CuInS$_2$ thin films prepared using single-source thermal evaporation method was investigated by Akaki et al.. Bi atoms enhances the growth of CuInS$_2$ single phase at lower temperature and the crystalline quality of doped films was higher compared with the non-doped ones [56]. Zribi et al. investigated the post-growth annealing treatment effects on properties of Na-doped CuInS$_2$ thin films grown by double source thermal evaporation method. Vacuum annealing was performed on the films from 250 to 500 °C. On annealing above 350 °C, traces of Cu and In$_6$S$_7$ in the films disappear. Good quality CuInS$_2$: Na 0.3 % films were obtained on annealing at 500 °C. The absorption coefficient of Na-doped CuInS$_2$ thin films reached 1.5 x 10$^5$ cm$^{-1}$. Band gap of the doped samples annealed in the temperatures from 250 to 500 °C was in the range 0.038–0.105 eV [57]. Rabeh et al. studied structural, optical and electrical properties of undoped and Sb-doped CuInS$_2$ thin films grown by single source thermal evaporation method on corning glass substrates heated at 100 °C. Quantity of the Sb source was determined to be in
the range 0-4 wt % molecular weight compared with the CuInS$_2$ alloy source. Effect of annealing atmospheres on the properties of the films was studied. Sb doped CuInS$_2$ possess relatively high absorption coefficient between $2 \times 10^4$ cm$^{-1}$ and $10^5$ cm$^{-1}$ in the visible and near-IR spectral range. Sb-doped CuInS$_2$ thin films exhibit p-type conductivity and air annealing resulted n-type conductivity [58]. Structural and optical properties of non-doped and Sn-doped CuInS$_2$ thin films grown by using double source thermal evaporation method were studied by Rabeh et al.. Vacuum annealing was performed on these films at a temperature of 250 °C. After annealing polycrystalline CuInS$_2$ films were obtained and no Sn binary or ternary phases were observed for the deposition time of Sn (by evaporation from a thermal evaporator) less or equal to 5 min. The band gap of Sn-doped samples after annealing was in the range 1.45–1.49 eV and they exhibited n-type conductivity after annealing [59]. Zn-doping was also performed in CuInS$_2$ thin films grown with the help of double source thermal evaporation method. Vacuum annealing was performed on these films at 260 °C for 2 hours. The Zn-doped samples had band gap energy of 1.46–1.58 eV and they exhibited p-type conductivity. Zn species can be considered as suitable candidates, for use as doped acceptors to make CuInS$_2$-based solar cells [60].

Three- source evaporation technique is employed for depositing good quality CuInS$_2$ thin films. Both p and n-type films were prepared. By replacing sulphur source by an H$_2$S gas source equipped with mass flow control helped to improve the sulphur deposition further, which is regarded as the most critical factor in the stoichiometry control. Resistivity of the films was between 0.01 and 10 Ω.cm and the grain size was between 2 and 8 μm. Electron mobility (21.84 cm$^2$V$^{-1}$s$^{-1}$) and hole mobility (1.42 cm$^2$V$^{-1}$s$^{-1}$) of these samples are higher than those reported for samples prepared with other methods [61]. CuInS$_2$ thin films were also deposited using MBE type evaporation of the
elements on (100) Si and glass substrates. This three-stage source combines excellent focusing characteristics with the option of thermally cracking large sulphur molecules. Crystal quality of the films can be improved by depositing on heated substrates but these films show a pronounced island formation [62].

Guillen et al. prepared CuInS$_2$ thin films by ‘rapid thermal annealing’ at 350 °C. Binary sulfide precursors evaporated at a substrate temperature lower than 200 °C were compared with CuInS$_2$ layers prepared directly by evaporation on to 350 °C heated substrates. X-ray Diffraction (XRD) and XPS measurements on these films showed similar structure and chemical characteristics. Some morphological variations are observed in atomic force microscopy analyses of the two samples. Differences in the optical absorption for these samples can be co-related with atomic force microscopy (AFM) analyses. Fermi level for both samples were a little below the middle of the gap, as corresponds to almost ideal composition [63]. Akaki et al. annealed evaporated CuInS$_2$ films in H$_2$S atmosphere from 250 to 500 °C for 60 min. It was observed that all the films annealed above 350 °C were of CuInS$_2$ single phase, regardless of the Cu/In ratio of the source material. Carrier concentration, resistivity and carrier mobility of these films (Cu/In ratio-1.5) were approximately $1 \times 10^{21}$ cm$^{-3}$, 0.1 $\Omega$.cm and 0.1 cm$^2$/Vs respectively at room temperature. By using source material having Cu/In ratio 1.5, the films are Cu-rich and Cu/In ratio was 1.37 in the sample. Cu rich films i.e., Cu/In ratio of 1.5 shows larger grain size and roughness than those of the films prepared from the Cu/In ratio of 1.0 [64]. Neisser et al. studied effect of Ga incorporation in sequentially prepared CuInS$_2$ thin films. Thin films of CuInS$_2$: Ga was prepared by sequential evaporation of Cu-In-Ga precursors and sulfurization in sulfur vapor. The resulting compound was CuGa$_x$In$_{1-x}$S$_2$, depending on overall Ga content and sulfurization temperature. This quaternary compound formed exhibited a change in absorber lattice constant
and band gap. Open-circuit voltages well above 800 mV and fill factor of 71% could be achieved by using this absorber layer [65]. Akkari et al. used oblique angle deposition technique for depositing CuInS$_2$ films onto substrates submitted to a thermal gradient. Resulting films showed an improvement in the optical properties i.e., high absorption coefficient ($10^5 - 3 \times 10^5$ cm$^{-1}$) in the visible range and near-IR spectral range. SEM analysis proved that the films had microstructure with columns that were progressively inclined as the incident angle was increased [66]. Akaki et al. doped Sb in CuInS$_2$ thin films grown by single source thermal evaporation method. The films were annealed from 100 to 500 °C in air after the evaporation. Polycrystalline films were formed on annealing Sb doped CuInS$_2$ films above 200 °C with band gap energy of 1.43–1.50 eV. Sb-doped CuInS$_2$ thin films are close to stoichiometry in comparison with undoped CuInS$_2$ thin films [67].

He et al. deposited CuInS$_2$ films on float glass substrates by a reactive radio frequency sputter process using Cu–In inlay target (Cu metal disc inlayed by indium) and H$_2$S gas in one step. The In/Cu ratio in films was much less than one although its ratio was nearly one in the target. Different sputter yield of indium and Cu, the presence of an additional layer covering the surface of the In inlay due to the reaction of H$_2$S and In inlay during sputtering are responsible for this. The sputtered film consisted of CuS, Cu$_2$S, and CuInS$_2$ phases. Hole concentration of the ‘as deposited’ Cu-rich ‘CIS’ films range between $3.55 \times 10^{17}$ cm$^{-3}$ and $1.58 \times 10^{19}$ cm$^{-3}$, for temperatures between 77 and 350 K. Carrier concentration in the films could be tuned from $10^{19}$ to $10^{17}$ cm$^{-3}$ by using Cu–In alloy target [68]. He et al. also reported the deposition of high quality CuInS$_2$ films with a fixed radio frequency power of 200 W on bare float glass substrates at a substrate temperature of 400 °C or above. H$_2$S flow was in the range of 20–30 sccm. As-sputtered films are highly (112) oriented with rougher surface, mainly due to incoherent top layer of Cu$_x$S precipitate.
The as-grown films sputtered at 500 °C have an optical bandgap of 1.44 eV. Resistivity, carrier concentration, Hall mobility of the films sputtered at 400 °C are approximately $2 \times 10^3 - 10^4 \ \Omega \cdot \text{cm}$, $3 \times 10^{14} - 10^{15} \ \text{cm}^{-3}$ and 2–20 $\text{cm}^2/\text{V s}$ respectively [69].

Cayzac et al. reported deposition of crystalline chalcopyrite CuInS$_2$ thin films employing RF sputtering at room temperature using crystalline CuInS$_2$ target. The process does not involve any subsequent toxic gas, chemical or heat treatment. XRD studies indicated that until a critical thickness is reached the films are amorphous in nature and after that, they transform into crystalline chalcopyrite films with preferential (112) orientation with average grain size of 25–100 nm. At low deposition rates, smooth films were obtained. As the deposition rates increased by increasing RF power, rougher films covered with surface particles were formed. In order to avoid In$_2$S$_3$ and Cu$_2$S phases in the deposited films, the target preparation is essential. Hall measurements showed that the films were p-type with bulk carrier density about $10^{18}/\text{cm}^3$ [70]. Seeger et al. deposited good quality CuInS$_2$ absorber layers through reactive magnetron sputtering process from copper and indium targets in Ar/H$_2$S sputtering atmosphere. The intrinsic electronic quality of the films was excellent, allowing the preparation of CuInS$_2$ cells with efficiency of 11.4 % and open circuit voltage of 745 mV. However the reproducibility of the device is low. Deposition rate from the indium target decreased by about a factor of two, while that from the copper target only by about 20 %. This decreasing content of indium in the first deposition step lead to an open, ‘porous’ CuInS$_2$ film morphology which was responsible for shunting problems between back and front contact of the solar cell. For stable CuInS$_2$ film deposition process an in-situ control of the Cu/In ratio and the film morphology is advisable [71]. Liu et al. reported preparation of CuInS$_2$ films with the help of reactive sputtering together with vacuum rapid annealing. These films consisted of single
chalcopyrite phase with preferential crystalline orientation along (112). EDAX measurements showed the constituent ratio [Cu+In]/[S] and [Cu]/[Cu+In] of about 1 and 0.5 respectively. Fourier transform infrared spectrometer analysis revealed that all CuInS₂ films had good homogeneity in shape and size of the grains and in distribution of constituent and defects. The deposition method followed in this study is beneficial to promote genuine realization of the large-scale production of the ultra-high efficiency Cu-III-VI₂ thin film solar cells [72].

Ogawa et al. prepared chalcopyrite CuInS₂ by sulfurization of a layered metallic precursor at 550 °C in argon containing H₂S. The Cu/In ratio in the film was varied from 0.8 to 1.85. It was observed that the resistivity of the film decreased by aging in air and it can be attributed to gas absorption in the film which gives rise to an increase in the hole mobility. Also resistivity of the films increased by annealing in vacuum or in air and it is due to gas desorption. The hole concentration of the films was independent of aging and was in the order of 10²⁰ cm⁻³. The article discussed electrical conduction in the thin film in terms of hole transport crossing over an inter-granular potential barrier in the polycrystalline film [73]. Wada et al. developed a two-stage process for CuInS₂ deposition which comprised of a first process by which Cu-In-O films are prepared from Cu₂In₂O₅ target by pulsed laser deposition. The prepared Cu-In-O films were transformed into CuInS₂ films by applying an annealing in a H₂S gas. On annealing the films at a temperature higher than 400 °C, chalcopyrite CuInS₂ is obtained. This process is applicable to prepare CuInSe₂ thin films also by annealing Cu-In-O film in H₂Se atmosphere [74]. Antony et al. reported the deposition of single-phase CuInS₂ thin films with chalcopyrite structure by the two-stage processes which involved the preparation of Cu₁₁In₉ alloy by annealing the evaporated copper and indium bilayers followed by the sulphurisation. Sulphurisation temperature was optimized as 350 °C for three hours, which resulted in single-phase p-type chalcopyrite CuInS₂ films with a
band gap of 1.45 eV. These films were ideal for the application as absorber layer in solar cells [75].

Solvothermal route was also employed for the deposition of CuInS$_2$ thin films in ethylene glycol under the open-air condition. Copper chloride, indium chloride and thiourea were the starting materials. It was observed that the products were significantly affected by the reaction time, temperature and the diffusion of the reactors [76]. Tang et al. developed an in-situ growth strategy for preparing CuInS$_2$ films by solvothermally treating flexible Cu foil in an ethylene glycol solution containing InCl$_3$.4H$_2$O and thioacetamide with a concentration ratio of 1:2. Higher solvothermal temperature is favorable for the growth of CIS films with higher crystallinity. Morphology of the deposited films was controlled by the reactant concentration. If InCl$_3$.4H$_2$O concentration is relatively low (≤ 0.042 M), single-layered CIS films composed of high ordered potato chips shaped nanosheets were formed; otherwise, it preferred to form a double layered film, for which the lower layer was similar to CIS ordered nanosheets while the upper layer was composed of flower shaped superstructures. All these CIS films possessed direct bandgap energy of 1.48 eV. Single-layered CIS films on Cu foil were employed for fabricating flexible solar cells with a structure of Cu foil/CuInS$_2$/CdS/i–ZnO/ITO/Ni–Al, which showed power conversion efficiency of 0.75 % [77].

Lee et al. employed sol–gel spin-coating method for depositing chalcopyrite CuInS$_2$ thin films, using copper acetate monohydrate (Cu(CH$_3$COO)$_2$.H$_2$O), dissolved in 2-propanol, and indium acetate (In(CH$_3$COO)$_3$) in 1-propanol. The two solutions were mixed to form the starting solution. Solution was dropped onto glass substrate, rotated at 1500 rpm and dried at 300 °C for Cu–In as-grown films. In the next step, the films were sulfurized inside a graphite container box. Raman spectra measurement confirmed that Cu–S or In–S compounds were not formed in the thin films [78].
Shi et al. reported deposition chalcopyrite CuInS$_2$ ternary films using successive ionic layer adsorption and reaction (SILAR) method on glass substrates at room temperature and heat-treated under Ar atmosphere at 500 °C for 1 h. Solution containing mixture of CuCl$_2$ and InCl$_3$ with different ionic ratios ([Cu]/[In]) were used as cation precursor and Na$_2$S as the anion precursor. Stoichiometric CuInS$_2$ film was obtained by adjusting [Cu]/[In] ratios in solution. Nearly stoichiometric composition of CIS films was obtained from the solution with the [Cu]/[In] range from 1 to 1.25, while [S$^{2-}$] concentration kept at 0.05 mol/L and they possess a band gap of 1.45 eV. Resistivity of these films decreased with increase of [Cu]/[In] ratios. As the [Cu]/[In] increased from 1 to 2, the films showed wide range of resistivity down from 80.5 to 3.4 x 10$^{-3}$ Ω.cm. This is due to the formation of high conductivity Cu$_{2-x}$S phase in the grains [79]. Shi et al. also investigated the effect of hydrothermal annealing (at 200 °C) in Na$_2$S solution on CuInS$_2$ thin films deposited by SILAR method. Well-crystallized CuInS$_2$ films could be obtained after annealing in 0.1 mol/L Na$_2$S solution for 1.5 h. Annealing was carried out in a sealed teflon-lined autoclave. Sulfur rich films resulted after annealing and they showed direct band gap varied from 1.32 to 1.58 eV as the annealing time increased from 0.5 h to 2 h [80].

Penndorf et al. developed a new technique, “CISCuT”, for the preparation of polycrystalline single-phase CuInS$_2$ thin films for solar applications in a continuous roll-to-roll process. In the first step, a copper tape is electrochemically plated with an indium layer. In the second step, this tape was made to undergo a rapid sulfurization process at a temperature (600 °C) and at an atmospheric pressure to form CuInS$_2$ thin films. Solar cells fabricated from this material showed efficiencies around 6 %. This low cost, continuous growth process without any vacuum set up is possibly a way to make solar cell and module production competitive with conventional energy generation [81].
Winkler et al. reported a consistent view of the compositional depth profile and phase content of CISCuT films produced under special conditions. $\text{Cu}_2\text{S}_x$ phase was removed by KCN etching. The CuInS$_2$ and CuIn$_3$S$_8$ layers in the films were under compressive and tensile stress respectively. Oxygen was observed to be a major contamination in the films [82].

Podder et al. reported deposition of CuInS$_2$ thin films on ITO glass substrate by a two-step process using a simple, low-cost, photochemical deposition and subsequent annealing. For InS thin films aqueous solution of In$_2$(SO$_4$)$_3$ and Na$_2$S$_2$O$_3$ were used. Cu$_k$S films were deposited on the InS films from CuSO$_4$ and Na$_2$S$_2$O$_3$ and the films were annealed at 300 °C for 30 min. Inter diffusion of Cu and In occurs during the annealing. Composition of the annealed films was determined by the deposition time of the binary layers. By optimizing the conditions, nearly stoichiometric CIS with band gap energy of about 2.2–2.3 eV was obtained [83].

‘Paste coating’ method was also reported for CuInS$_2$ absorber layers. Precursor powders i.e., CuInS$_2$ and CuS were synthesized by a solvothermal method. Ethyl cellulose and phosphate ester were used respectively as a resin and a dispersant and dihydroterpineol was used as solvent to dilute these. Screen printing method was used to distribute the paste on Mo-coated soda-lime glass substrate. It was difficult to obtain the densification of the CuS-doped CuInS$_2$ layer with only sulfurization. On introducing oxidation process before sulfurization led to quite dense CuInS$_2$ layer. On oxidation the chalcopyrite phase nearly broke down but the phase was restructured with the sulfurization [84].

Metzner et al. epitaxially grew CuInS$_2$ films with typical thickness of 100 nm on sulphur-terminated Si wafers of (001) and (111) orientation and on single-crystalline CaF$_2$ substrates using three-source molecular beam epitaxy
(MBE). Transmission electron microscopy (TEM) analyses shows that, metastable Cu-Au ordering on the cation sub lattice was found to be the dominating structure in the films deposited on Si (001) at medium temperature (300 °C). Electronic states deep in the CuInS₂ bandgap can be successfully removed by post deposition treatments in hydrogen and air at elevated temperatures up to 400 °C. Excess indium in the films leads to the formation of In₂S₃ and CuIn₅S₈ as minor phases. CuS segregates were formed at the surface of Cu-rich samples and could be removed by etching [85].

Qiu et al. deposited CuInS₂ thin films by ‘ion layer gas reaction’ (ILGAR) method using C₂H₅OH as solvent, CuCl and InCl₃ as reagents and H₂S gas as sulfuration source. The chalcopyrite CuInS₂ with near stoichiometry can be deposited with [In³⁺] ≤ 0.05M and [Cu⁺] ≤ 0.078M. Further increase in cationic concentration resulted in CuₙS segregation phase. CuInS₂ thin film deposited from lower cationic concentration was uniform, compact and good in adhesion to the substrates. With the increase in precursor concentrations the optical band gap decreased (1.40-1.30 eV) slightly along with dark resistivity (50 to 10 Ω.cm). The carrier concentration and hall mobility increased as the mixing precursor concentration increased [86]. Das et al. also reported the deposition of nanostructured CuInS₂ thin films using ILGAR process. Cu and In precursors were deposited on glass substrate through coating technique and annealed in H₂S atmosphere at different temperatures [87]. Camus et al. prepared CuInS₂ thin films employing spray ILGAR. Several post deposition treatments were applied to the deposited films. Composition and surface chemistry the ILGAR films were very similar to device grade reference samples prepared through rapid thermal processing [88].

Hou et al. deposited uniform CuInS₂ films employing electrostatic spray assisted vapor deposition (ESAVD) method. Copper nitrate and indium
nitrate salts were dissolved into a thiourea-based water/alcohol solution is the precursor solution. Film showed chalcopyrite crystalline structure with preferred (112) orientation. Depending on the precursor composition and processing parameters, bandgap varied from 1.40 to 1.49 eV. CdS/CulnS$_2$ heterojunction was also produced on an ITO glass substrate having good photovoltaic response [89].

Yukawa et al. prepared CulnS$_2$ thin films with the help of electrodeposition without usual heat treatment in H$_2$S atmosphere. Acidic aqueous solution containing CuSO$_4$, In$_2$ (SO$_4$)$_3$ and Na$_2$S$_2$O$_3$ at -0.9 V vs Ag/AgCl for 300-1200 s was used for film deposition. Single phase CulnS$_2$ films were obtained at pH about 1.5 by the proper adjustment of the Cu$^{2+}$/In$^{3+}$ ratio, with the concentration of Na$_2$S$_2$O$_3$ fixed at 400 mM. Well-crystallized films were obtained by annealing in vacuum at 673 K. Films prepared were non-stoichiometric with tetragonal chalcopyrite type structure. Conduction type changed from p to n in the indium-rich region [90]. Asenjo et al. also reported CulnS$_2$ preparation by one-step electrodeposition using the same precursors. Electrochemical quartz crystal microbalance (EQCM) was used to study the growth of CulnS$_2$ films [91]. Martinez et al. reported preparation and characterization of Cu–In–S thin films on stainless steel by electrodeposition technique using an electrolytic bath consisting of metal salts dissolved in a buffer solution. Films were annealed in N$_2$ atmosphere to improve crystallinity. Band gap of the films is close to 1.5 eV [92]. CulnS$_2$ thin films for the application in solar cells were also grown on Ti substrates by electrodeposition and sulphurisation. Composition of the CulnS$_2$ films was mainly determined by the Cu/In atomic ratio of initial Cu–In precursor [93].

Hwang et al. reported growth of CulnS$_2$ layers on GaP substrates by the metalorganic chemical vapor deposition (MOCVD). Hydrogen sulfide gas
together with the vapors of CuCl(NCCH₃)₆ and InCl₃(NCCH₃) were used as transport agents. X-ray analysis confirmed the formation of single phase CuInS₂ epitaxial layer on the substrate. Energy dispersive X-ray analysis (EDAX) and Rutherford back scattering (RBS) confirmed the existence of Cu and S in the films [94]. Harris et al. deposited copper indium disulfide films using spray chemical vapor deposition at atmospheric pressure. Temperature for deposition was 390 °C using [(PPh₃)2CuIn(SEt)4] as a single source precursor in argon atmosphere. The films exhibited crystallographic gradient, with the leading edge having (220) preferred orientation and the trailing edge having (112) orientation. Films with the best electrical properties were annealed at 600 °C following deposition at 390 °C. It was observed that prolonged exposure of the films to the electrolyte decreased photo response. Solar cells were fabricated with CuInS₂ having the structure Al/ZnO/CdS/CuInS₂/Mo/Glass and it showed an efficiency of 0.68 %, for a 0.5 cm² cell under simulated AM0 illumination [95].

Djessas et al. deposited copper indium disulfide thin films for photovoltaic applications by close-spaced vapor transport in a vertical reactor closed under vacuum. Solid iodine was used as reagent. Compared to other I-III-VI compounds the stoichiometry temperature range is relatively large: the lower limit (∼ 370 °C) corresponds to the formation of CuI in the layers and the upper limit (∼ 680 °C) is imposed by the glass substrate. Within this temperature range no phase change was observed. All the layers are p-type, with carrier densities of the order of 10¹⁶ cm⁻³ [96].

Cui et al. reported the deposition of non-crystalline CuInS₂ thin films on ITO coated glass by one step chemical bath deposition (CBD) in acidic conditions. For the deposition of CuInS₂ thin films, solutions of CuSO₄, InCl₃ and Na₂C₆H₅O₇ were used. With the addition of HCl, pH of the solution was maintained at approximately 3.5–4.5. Deposition temperature was 45 °C and
deposition time was 2 hour. Under continuous stirring thioacetamide was also added in the solution. Polycrystalline CuInS$_2$ films were obtained after sulfuration of the films in sulfur atmosphere at 450 °C for 1.5 h. These films were p-type and the carrier concentration was 1.68 x $10^{16}$ cm$^{-3}$ and band gap was about 1.45 eV [97].

Nanu et al. deposited CuInS$_2$ thin films employing atomic layer deposition (ALD) over glass, TCO glass, and TiO$_2$ substrates using CuCl, InCl$_3$ and H$_2$S as reactants. For the deposition, pressure was in the range 2-10 mbar and temperature was between 350 °C and 500 °C. It was observed that composition of the films depended on the length of CuCl pulse. Microstructure and homogeneity of the films improved on increasing reaction temperature. Depending on deposition conditions single phase, Cu-poor and Cu-rich CuInS$_2$ films are formed. Also, no chloride impurity was detected in the films which indicated the complete reaction between the metal chloride and H$_2$S [98]. Lin et al. employed electrochemical atomic layer deposition (EC-ALD) for depositing CuInS$_2$ on gold substrate at room temperature. Optimum deposition potentials for each element were determined using cyclic voltammetry (CV) technique. Amperometric I–t method was employed to prepare the semiconductor compound. Films had (112) preferred orientation and Cu, In, S are present in an atomic ratio of approximately 1:1:2. Also these films were composed of particles with uniform grain size fell into nano-range. Band gap of this film was 1.50 eV as measured using FT-IR [99].

Chemical spray pyrolysis is already proved to be a simple, low cost chemical deposition technique for device quality CuInS$_2$ thin films. Generally used precursors for CuInS$_2$ deposition contain CuCl$_2$, InCl$_3$ and thiourea [100-102]. Instead of chloride based precursors, deposition of CuInS$_2$ by nitrate based precursors are also reported [103]. Cu/In ratio in the precursor solution and substrate temperature are the two important factors that controls the
structural, optical and electrical properties of CuInS₂ thin films [45, 104, 105]. Generally Cu rich films are suitable for photovoltaic applications [106]. Deposition temperature was between 300 to 350 °C for good quality CuInS₂ films [102,103]. A variety of substrates like glass, alumina, metal oxide and polymer substrates can be used to deposit CuInS₂ by spray pyrolysis [107-110]. Nature of substrate can affect the growth and structure of as deposited films. The crystal structure of CuInS₂ films deposited using CSP technique are either sphalerite or chalcopyrite structures and sphalerite structure changes to chalcopyrite on annealing [111]. It was observed that on post deposition annealing of CuInS₂ films in H₂S atmosphere, crystallinity and stoichiometry of the films improved. Optical band gap increased and there was an adverse effect on electrical properties of the films [112]. On incorporating Na in sprayed CuInS₂ crystallinity, band gap, conductivity and photosensitivity of the films improved. Na₂S can be added in the precursor solution as dopant [113]. Incorporation of Al and Mn in sprayed CuInS₂ had also been reported. On Mn doping in sprayed CuInS₂ band gap increases [114].

1.9.2 Review on CuInS₂ based solar cells

The maximum reported efficiency for CuInS₂ based thin film solar cell is 12.5 % by Klaer et al.. Molybdenum was the back contact and CuInS₂ absorber was deposited using dc magnetron sputtering and sulphurization. Heterojunctions were then prepared by chemical bath deposition of 50 nm CdS and sputtered transparent conducting ZnO window layer. Aluminium grid was used for contacting and MgF₂ was the antireflection coating over the cell. They observed that solar cell performance decreased only slowly for small deviations of the Cu/In ratio from the optimum value [15]. Goto et al. reported 13 % efficient thin film solar cell by following TCO/CdS/CuInS₂/CuGaS₂ structure. For absorber layer deposition, vacuum evaporation and sulphurization was employed. Buffer layer was chemical bath deposited CdS
and for TCO, RF sputtered In$_2$O$_3$ layer was used. They concluded that the improved characteristics of the cell arise due to high crystallinity and electron barrier of the hetero-structure consisting of CuInS$_2$ absorber layer and thin CuGaS$_2$ base layer [115]. Hengel observed improvement in open circuit voltage ($V_{oc} > 800$ mV) in CuInS$_2$ thin film solar cells by incorporating Ga in CuInS$_2$. They employed sequential technique for the preparation of CuInS$_2$: Ga/CdS/ZnO cells having efficiency of 11.6 % [116].

Scimer et al. reported 11.4 % total area efficiency ($A = 0.5$ cm$^2$) CuInS$_2$ solar cells from rapid thermal process (RTP). They followed glass/Mo/CuInS$_2$/CdS/ZnO cell structure. Vapor pressure of sulfur and its constancy during the process has an important influence on device quality [117]. Braunger et al. reported 11.4 % efficient polycrystalline CuInS$_2$ thin film solar cell having Cd-free buffer layer [In$_x$(OH,S)$_y$]. CuInS$_2$ was deposited by thermal evaporation. They concluded that the choice of the buffer layer strongly influences the electrical characteristics of the heterojunction through light induced secondary transport paths [118]. CuInS$_2$ thin films, prepared through sulfurization of a metallic precursor, is used to form thin film solar cell with CdS which exhibits efficiency of 10.5 % deposited either on a Pt sheet or a Mo-coated soda lime glass substrate. Adhesion of CuInS$_2$ was significantly improved by introducing very thin Ga layer between the Mo surfaces and stacked Cu/In precursor layer [119]. Scheer et al. reported 10.2 % efficiency for solar cell prepared with copper-rich p-type CuInS$_2$ absorber prepared by thermal co-evaporation. The cell structure was glass/Mo/p-CuInS$_2$/n-CdS/n$^+$-ZnO/Al. For this configuration copper to indium ratio between 1.0 and 1.8 can be tolerated with small (< 10 %) solar-to-electrical conversion losses [120]. Lewerenz et al. fabricated new heterogeneous poly crystalline n-CuInS$_2$ based semiconductor which has yielded conversion efficiencies of 9.7 % in an electrochemical cell. Origin of the improved efficiency is attributed to impurity
scavenging by In spheres resulting from modified vapour/liquid/solid (VLS) growth process and the influence of the acidic iodine iodide electrolyte on the cell performances [121]. Using spray deposited CuInS$_2$/In$_2$S$_3$ heterojunction Teny et al. fabricated 9.5% solar cell on ITO substrates. Manual spray was used to deposit the cell. They were able to avoid the usual cyanide etching and CdS buffer layer, both toxic, for the fabrication of the cell [101]. Asenjo et al. fabricated CuInS$_2$/In$_2$S$_3$/ZnO type solar cells and the influence of CBD deposited In$_2$S$_3$ film properties on the behavior of the device was investigated. Maximum efficiency of 8.6% was reported. CuInS$_2$ films were grown on Mo substrate through sequential sputtering-evaporation process [122]. Sandino et al. analyzed Mo/CuInS$_2$/ZnS stacked layers, using high resolution transmission electron microscopy (HRTEM) and used it for the fabrication of solar cells with Mo/CuInS$_2$/ZnS/TCO structure. CuInS$_2$ was prepared by co-evaporation and efficiencies of 7.8% and 5.4% were attained using evaporated and CBD deposited ZnS buffer layers [123]. One dimensional CuInS$_2$–ZnS hetero-structured nanomaterials synthesized by ‘seed-assisted’ synthetic route were used as the counter electrodes of dye sensitized solar cells. Shapes of hetero-structured nanorods could be tuned from burning torch-like to longer rod-like by varying the concentration of added indium. Dye-sensitized solar cells (DSSCs) using these hetero-structured nanocrystals exhibited power conversion efficiency (7.5%) superior to DSSCs made with conventional platinum electrode (7.1%) under the same device configuration [124].

An efficiency of 7% was reported by Goossens et al. for spray deposited CuInS$_2$ solar cells. Here spray deposited TiO$_2$ was used as the nanoporous electron conductor and sprayed In$_2$S$_3$ was the buffer layer. Transient absorption spectroscopy was employed to make an accurate assessment of the fundamental electronic processes that are involved in CuInS$_2$ absorber layer and electronic states in the band gap related to the presence of
anti-site defects. The population lifetime of electrons in deep states was large and these states acted as electron traps rather than recombination centers. Upon irradiation, electrons were stored, leading to space-charge formation. The low open circuit voltage \(V_{oc}\) of CuInS\(_2\) cells as well as the crossover of the current-voltage curves is due to this temporal storage of charge [125]. Luo et al. reported simple aqueous solution route to prepare mercaptoacetic acid attached CuInS\(_2\) quantum dots. Using this material, core-shell CuInS\(_2\)-Mn doped CdS quantum dot sensitized solar cells were assembled and it showed power conversion efficiency of 5.38 % [126].

Okuda et al. reported fabrication of buffer-free CuInS\(_2\) solar cells having 5.5 % efficient with transparent conducting Zn\(_{1.8}\)Mg\(_3\)O:Al films. They eliminated CdS buffer layer from typical ZnO:Al/CdS/CuInS\(_2\)/Mo/glass type solar cells. ZnO:Al was replaced with (Zn,Mg)O:Al layer prepared by co-sputtering ZnO:Al and MgO:Al for conduction band offset matching. The junction quality, deteriorated by sputtering damage during (Zn,Mg)O:Al deposition; this was recovered by post annealing after cell fabrication. Low \(V_{oc}\) of as-fabricated cells of 0.25 V was improved to 0.52 V by annealing at 250 °C for 10 min, leading to an improvement in efficiency from 1.9 to 5.5 % [127]. 3D solar cell concept was used by Nana et al. for fabricating solar cells with TiO\(_2\)/CuInS\(_2\) nanocomposites with efficiency of 4 %. Here nanometer scale inter penetrating network was formed by infiltrating CuInS\(_2\) inside the pores of n-type TiO\(_2\) by atomic layer chemical vapor deposition. Al\(_2\)O\(_3\) inter layer was used for suppressing Cu diffusion and In\(_2\)S\(_3\) was used as the buffer layer. It was also observed that during deposition process, the stoichiometry of CuInS\(_2\) and TiO\(_2\) were modified and the stoichiometry was restored by thermal annealing in sulfur and oxygen [128]. Li et al. reported quantum dot-sensitized solar cell (QDSSC) with 4.2 % efficiency which consisted of TiO\(_2\)/CuInS\(_2\)-QDs/CdS/ZnS photo anode, polysulfide electrolyte, and CuS counter electrode.
CuInS₂ deposited by spin coating method was also used to fabricate solar cells with 3.99% efficiency. Post deposition treatment was also carried out at 250 °C in inert atmosphere [130].

Kazmerski et al. reported CuInS₂ thin-film homojunction solar cells having an efficiency of 3.62%. CuInS₂ films were grown employing dual-source deposition technique. Forward dark J-V characteristics indicated that recombination-generation mechanism at the junction dominated device operation. The devices had stability but materials-related problems limited the device performance of this solar cell [131]. Rath et al. fabricated nanocomposite CuInS₂/PSiF-DBT solar cells with conversion efficiency of 2.8%. Spin coating was used for solar cell fabrication [132]. Chang et al. fabricated Cu₂S–CuInS₂–ZnSe quantum dot (QD)-sensitized solar cell having efficiency of 2.52%. CuInS₂ sensitizer, Cu₂S buffer layer and ZnSe passivation layer were fabricated through SILAR process. The band edges of the Cu₂S–CuInS₂–ZnSe in the QD-sensitized solar cell generated stepwise cascade, which promoted the separation of excited electrons and holes across the interfacial region [133].

Krunks et al. deposited extremely thin absorber layer (ETA) solar cells through spray pyrolysis method. Spray deposited ZnO nanorod layer (ZnOₙ) was used for ITO/ZnOₙ/InS₃/In₂S₃/CuInS₂ solar cells having an efficiency of 2.5%. In this type of ETA solar cells, p-n junction area is increased very much when comparing with flat structure and this increased short-circuit current density. Preparation technology is simple, fast and operates at low or moderate temperature; hence it could be possible to fabricate efficient solar cells with large area at low cost using this structure [134]. Weil et al. reported the fabrication of CuInS₂ solar cells by air-stable ink rolling. The ink for CuInS₂ consists of elemental sulfur, Cu(acac)₂, and In(acac)₃ (acac = acetylacetonate)
dissolved in pyridine. CdS was the buffer layer used and it was deposited through chemical bath deposition. ZnO (TCO) layer was deposited using reactive DC magnetron sputtering. Power conversion efficiency of the fabricated device was 2.15 % [135]. Tiwari et al. fabricated all-sprayed CuInS$_2$/ZnO solar cells with an efficiency of 2 %. Indium-doped ZnO films are essential for better photovoltaic response and [In]/[Zn] atomic concentration ratio was 0.03 for the best device. Deposition of an interlayer of CuInS$_2$ and post-deposition annealing of junctions are essential for obtaining good quality solar cells. Multistep tunneling and recombination is the most likely mode of carrier transport in CuInS$_2$/ZnO heterojunctions [111].

Cho et al. synthesized monodispersed CIS nanocrystals by colloidal synthetic route and re-dispersed in toluene to form ‘ink’. CuCl, InCl$_3$, sulfur dissolved oleylamine (OLA) were used in the preparation of ink. This ink was applied to thin film solar cell devices with superstrate configuration by spray coating method. Device structure followed for the study was ITO/TiO$_2$/CdS/CIS/Au. TiO$_2$ and CdS were used as blocking layer and buffer layer respectively. Power conversion efficiency of 1.45 % was achieved by this device [136]. Ryo et al. fabricated superstrate type CuInS$_2$ solar cells by spray pyrolysis method. Glass/FTO/TiO$_2$/In$_2$S$_3$/CuInS$_2$ structure was followed for device fabrication. Crystallinity of the spray-deposited CuInS$_2$ films was generally good and its band gap value of was ~ 1.3 eV. For CuInS$_2$ films with thickness < 2 μm there was only one layer and had good adhesion. But CuInS$_2$ films with thickness > 3 μm were having several layers, and were easily peeled off during deposition. The best cell obtained had efficiency of 1.7 % [137]. Polymer/CuInS$_2$ hybrid solar cells and modules on flexible plastic substrate were also reported. Device fabrication was based on the metal xanthate route and low temperature annealing. These hybrid solar cells were deposited on flexible PET foils, which showed efficiency of 1.6 % [138].
1.9.3 Deposition of Cu$_2$S thin film

A variety of deposition techniques like chemical spray pyrolysis, electrodeposition, chemical bath deposition, sputtering, SILAR, chemical vapor deposition and solvothermal technique were already reported for Cu$_2$S thin films. Wang et al. employed asynchronous-pulse ultrasonic spray pyrolysis technique for the deposition of Cu$_x$S (x = 1, 2) thin films on glass from CuCl$_2$ and thiourea. Film deposition was at relatively low temperature without any complexing agent. The deposited Cu$_2$S films were a mixture of amorphous and polycrystalline phases. The crystalline phases of the films were highly depended on the molar ratio of thiourea to CuCl$_2$ and the pyrolysis temperature. Presence of both “covellite CuS” and “chalcolite Cu$_2$S” were confirmed by XRD and XPS analysis. Raman shifts for CuS phase was at 474 cm$^{-1}$ and that of Cu$_2$S phase was at 472 cm$^{-1}$ [139].

Isac et al. deposited copper sulfide (Cu$_x$S, x = 1.8–2) thin films through spray pyrolysis method. Aqueous and alcoholic solutions, containing CuCl$_2$ and thiourea were used as precursors. Deposition temperature was maintained at 285 °C. By controlling precursor solution composition and deposition parameters, dense, relative homogenous and uniform films of Cu$_2$S were obtained. Deposited films were chemically close to chalcocite (Cu$_2$S) or to mixtures of copper-rich phases (Cu$_2$S, Cu$_{1.8}$S, Cu$_{1.9375}$S) in which chalcocite or digenite (Cu$_{1.8}$S) were predominant. By optimizing spray time and modifying precursor solution concentration, using mixtures of water: ethanol: glycerin as solvents, morphology of the deposited films can be tailored. For the deposition of Cu$_2$S, the optimum precursor solution has Cu:S molar ratio of 1:3 in a water: ethanol: glycerin solvent with the volume ratio of 7:2:1. Spray time of more than 40 min at 285 °C are also preferred [140]. Davis et al. synthesized Cu$_2$S nanocrystals using single precursor by employing aerosol spray pyrolysis.
Copper diethylidithiocarbamate in toluene was used as the precursor solution. The precursor is aerosolized and aerodynamically dragged through a tube furnace. Inside the tube furnace, the droplets are dried and nanocrystals are formed. Particle size was smaller than 20 nm. These particles were preferentially formed as digenite (Cu$_{1.8}$S); but at low furnace temperature, it was possible to produce chalcocite (Cu$_2$S, p-type) nanocrystals, promising candidates for the development of low-cost, printable photovoltaic devices [141].

Grozdanov et al. employed electroless chemical deposition to deposit thin films of Cu$_2$S, Cu$_{1.8}$S, Cu$_{1.4}$S, and CuS on glass, polyester or metal substrates. Aqueous copper thiosulfate bath in acidic media was used for deposition. Deposited films differ in the optical transmission in the near infrared region, with Cu$_2$S being highly transmissive and CuS highly absorptive in the microwave radiation (i.e., in spectral range 0.8–2.5 μm). All films were p-type and highly conductive in nature. Conductivity increased from Cu$_2$S towards CuS [142]. A modified chemical deposition method was employed by Pathan et al. for the deposition of stoichiometric copper sulphide (Cu$_2$S) thin films. In this method the substrate was immersed into separate cation and anion precursor solutions and rinsing between every immersion with ion exchange water to avoid homogeneous precipitation. The cationic precursor was copper(II)sulphate pentahydrate (CuSO$_4$.5H$_2$O) solution complexed with mixture of 2N triethanolamine (TEA) and 2N hydrazine hydrate (HH). The pH of this solution was adjusted to ~5. Anionic precursor was sodium sulphide (Na$_2$S.H$_2$O) solution with pH ~ 12. For the preparation of stoichiometric, nanocrystalline Cu$_2$S, the preparative conditions such as concentration, pH of cationic and anionic precursors, adsorption, reaction and rinsing time durations, complexing agent, etc. were optimized. Absorbance of the film was 10$^4$ cm$^{-1}$ with direct optical band gap of 2.35 eV. Deposited films showed p-type conductivity and room temperature electrical resistivity was of the order of 10$^2$ Ω.cm [143].
Podder et al. deposited Cu$_x$S thin films ($x$ from 2.3 to 1.3) on ITO coated glass substrates by photochemical deposition from an aqueous solution of CuSO$_4$ and Na$_2$S$_2$O$_3$. pH was kept at 3 and photo irradiation was for the duration of 1–2 h. Thickness of the films was in the range of 0.15–0.35 μm. XRD studies showed polycrystallinity of the Cu$_x$S thin films and the energy band gap of the films were estimated in the range of 2.15–2.53 eV [144]. Bagul et al. deposited thin films of Cu$_x$S ($x$=1.0, 1.76, and 2.0) by solution growth technique (SGT) using thiosulfate, which acted as both complexing and sulfiding agent. The deposition parameters of Cu$_x$S such as pH of solution, deposition time, and deposition temperature were optimized. As the deposited films were amorphous, annealing was carried out in Ar atmosphere at 250 °C. Annealed films were polycrystalline in nature. Absorption coefficient varied in the range of $1 \times 10^5$ – $6 \times 10^5$ cm$^{-1}$. The optical band gap of Cu$_2$S was 2.48 eV [145].

Schimmel et al. reported the combined use of voltammetry and electrode illumination during anodic growth of Cu$_2$S and CuInS$_2$ films on copper substrates in KOH medium containing sulfur [146]. Anuar et al. employed cathodic electrodeposition for the preparation of Cu$_2$S thin film on Ti substrate. The process was carried out in presence of EDTA in aqueous solution. For Cu$_2$S films, they reported optimum deposition potential to be -0.40 V. In order to elucidate the electroodic processes that occur while potentials for electrodeposition were applied to determine the optimum potential for electrodeposition, cyclic voltammetry was carried out. The deposition bath consisted of CuSO$_4$ and Na$_2$S$_2$O$_3$ solution. Better photo activity was observed for samples prepared using higher concentrations of CuSO$_4$ compared to a fixed concentration of Na$_2$S$_2$O$_3$. For better films, the deposition period was 60 min and above. The band gap energy of these films was 1.50 eV [147].
Nair et al. deposited Cu$_2$S thin films using CBD on SnO$_2$/glass substrates. Chemical bath is constituted from copper(II)chloride, triethanolamine and thiourea at appropriate pH (10-12). These films were stable with respect to electrical and optical properties on storage under ambient conditions [148]. Allouche et al. deposited copper sulphide (Cu$_2$S) thin films through CBD technique. Depositions were carried out during deposition time of about 32.5 min in the pH range of 9.4 to 11. X-ray diffraction study showed that Cu$_2$S films exhibited the best crystallinity for pH = 10.2 and films grown on an SnO$_2$/glass substrate exhibited stoichiometric composition with [Cu]/[S] concentrations ratio equal to 2.02. The work function difference for the Cu$_2$S films deposited on SnO$_2$/glass substrates at the optimum pH value was found to be equal to 145 meV. Hall measurements confirmed the p-type electrical conductivity and electrical resistivity was of the order of $3.85 \times 10^4$ $\Omega$.cm. Band gap energy of the films is about 2.37 eV. Refractive index ($n$) and extinction coefficient ($k$) of the films varied in the range of 1.7–2.1 and 0.02–0.09 respectively. The optical properties of these films made them suitable for solar control coatings and photovoltaic devices [149].

Nomura reported preparation of copper sulfide thin layers by a single-source metal-organic chemical vapor deposition (MOCVD). This work deals with growth of high quality copper-deficient Cu$_{0.96}$S layers by low pressure MOCVD process using copper(II)bis(diethylthiocarbamate). Films were grown on Si (III), quartz, or glass substrates in horizontal hot-wall reactor made of quartz [150].

Pathan et al. employed (SILAR) method for depositing single phase of Cu$_2$S with hexagonal crystal structure using CuSO$_4$ and Na$_2$S. These films exhibited maximum transmittance ~ 53.4 % for $\lambda = 630$ nm. Absorption coefficient of the film was $10^4$ cm$^{-1}$. Film showed p-type conductivity with
band gap of 2.33 eV. Growth rate of the film was estimated to be 7 nm/cycle [151].

Das et al. prepared Cu$_2$S thin films of well-controlled thickness and stoichiometry by solid state reaction between CdS and CuCl films. Temperature range for this reaction was 200-250 °C. These films existed in the orthorhombic chalcocite phase and were utilized to fabricate Cu$_2$S/CdS solar cells. CdS films were prepared employing vacuum evaporation of pellets of CdS powder. Cu$_2$S films were deposited over CdS films by evaporating freshly prepared pure CuCl powder from a molybdenum boat. Growth of Cu$_2$S on CdS is topotactical. Chalcocite Cu$_2$S phase is obtained on reaction with both wurtzite and sphalerite structures of CdS [152].

Gorai et al. synthesized a series of stoichiometric and non-stoichiometric copper sulphides (Cu$_2$S, Cu$_{3+16}$, Cu$_{1.8}$S, Cu$_7$S$_4$, Cu$_{39}$S$_{28}$) via solvothermal route. Both ethylenediamine (En) and water were used as the solvent system at 130 °C. Solvothermal system consists of solvent, bivalent copper nitrate and thiourea. When the solvent was pure En, six-petal dendritic Cu$_2$S with central mid-ribs supporting each petal was observed. As the solvent was changed from pure En to (En + H$_2$O), dendrites were progressively broke to individual rods. For pure water as the solvent, spherical particles with a part of the surface covered with thin spaghetti-like form was observed. When pure En was used as the solvent, bidentate ligands En has connectivity with Cu ions, to which thiourea molecule also get attached. Partial reduction of Cu$^{2+}$ and breakdown of thiourea then occurs due to the elevated temperature and pressure of the solvothermal system, which resulted in dendritic or rod-like copper sulphides [153].

Cu$_2$S and CuS films were deposited by He et al. on float glass substrates using reactive RF sputter process with optimized sputter parameters,
such as power, temperature of the substrate, and the gas flow of the H$_2$S. XRD spectra showed that the Cu$_2$S films had (002) preferential orientation and both compounds had hexagonal structure. Hall-effect measurements indicated two activation energies related to the intrinsic defects in the Cu$_2$S films. CuS has relatively high carrier concentration around $10^{22}$ cm$^{-3}$, hence a much lower resistivity of about $10^{-4}$ Ω cm, and slightly lower Hall mobility of about 3 cm$^2$V$^{-1}$s$^{-1}$ compared with the semiconducting phase Cu$_2$S [154].

1.9.4 Review on Cu$_2$S based solar cells

Cu$_2$S possesses extremely favorable material characteristics for absorber layer in thin film solar cells. Cu$_2$S/CdS solar cell gained paramount promises and its history spans more than a half century, beginning in 1954, when Reynolds et al. first discovered photovoltaic response in heat treated Cu contacts on CdS at photon energies less than the CdS band edge [155]. Highest efficiency for Cu$_2$S based solar cell is 10.2 %, reported by Hall et al. for Cu$_2$S/Cd$_{(1-x)}$Zn$_x$S heterojunction. Here Cd$_{1-x}$Zn$_x$S film was deposited using thermal co-evaporation of CdS and ZnS from two-chamber concentric source onto a zinc-plated copper substrate at 210 °C. The zinc concentrations of the films were in the range of 0.1 $<$x$<$0.2. Before depositing Cu$_2$S over Cd$_{(1-x)}$Zn$_x$S surface, texturing of Cd$_{(1-x)}$Zn$_x$S film was done to improve light trapping characteristics of the device. Cu$_2$S layer was formed by reaction in a cuprous chloride solution. Gold was used as the front contact and Ta$_2$O$_5$ as the antireflection coating. Heat treatment at 170 °C in a flowing hydrogen atmosphere was also performed to improve light generated current and junction characteristics [156].

Bragagnolo et al. fabricated thin film CdS/Cu$_2$S cells having 9.15 % conversion efficiency. For cell fabrication, CdS was vapor deposited over Zn plated electroformed copper substrate. Heavily textured light-trapping Cu$_2$S
layer was topotaxially grown over CdS by reaction in a cuprous-ion solution. Very interestingly, a new technology to deposit the top grid and anti-reflection coating onto the Cu₂S and new analysis and processing techniques to separately measure and minimize fill factor losses have been developed in this work. Top electrical contact was formed by evaporating highly transmitting Au grid onto the Cu₂S surface. Finally an anti-reflecting SiO₂ quarter-wave coating was vapor deposited over the structure [16].

Saraf et al. synthesised Cu₂S and CdS nanoparticles through wet chemical method and Cu₂S/CdS solar cell was fabricated using spin coating technique. For solar cell fabrication, thin film of CdS nanoparticle approximately 100 nm in thickness was created using spin-coating technique on top of glass substrate and then thin film of Cu₂S nanoparticle (approximately 10 μm in thickness) was created on CdS thin film using the same technique. Silver was the back electrode. Efficiency of the fabricated cell approached around 10.9 % and fill factor around 73 % [157]. Cu₂S/CdS solar cells having efficiency of 7.6 % was fabricated by combining spray pyrolysis and evaporation. For device fabrication, solution containing cadmium was sprayed onto heated electrically conductive transparent substrate to form cadmium containing sulfide. Cuprous chloride powder was then vacuum evaporated onto the CdS crystals. By heating this Cu coated CdS layer during a time-temperature controlled cycle, a portion of the surface of the CdS crystals was converted to Cu₄S [158].

Ashour et al. fabricated glass/Ag/CdS/Cu₂S/Au solar cells having 7.2 % efficiency. The CdS layer was deposited using vacuum evaporation of pure CdS powder. The Cu₂S layer was produced by vacuum evaporation of thin layer of CuCl powder onto the CdS film at room temperature. Then the structure was heated at 170 °C for 5 min in the same vacuum chamber at pressure of 10⁻³ Pa. Here a layer of Cu₂S is formed by the topotaxial
conversion of some portion of CdS by CuCl. The major limitations for the present device were poor design of grid and high resistivity of CdS films [159]. Goldenblum et al. reported fabrication of large-area Cu$_2$S/CdS solar cells using vacuum evaporation technology alone. Successive vacuum deposition of chromium and silver over ordinary window glass at 200 °C served as the back contact. CdS layer was then vacuum evaporated over this using CdS powder. In the next step CuCl was vacuum evaporated over CdS and the samples were heated at 140 °C for 4 minutes. A solid state reaction take place and a layer of Cu$_2$S was grown topotaxially on the CdS surface. Methyl alcohol was used to wash off cadmium chloride produced by the reaction. High surface roughness of these films ensured high absorbance in the Cu$_2$S layer without any etching. The maximum efficiency of the device was 6.49 % at 100 mW/cm$^2$ [160]. Aperatthitis et al. reported all vacuum evaporated Cu$_x$S/CdS solar cells having efficiency in excess of 7 %. Copper sulphide layer was prepared by employing vacuum evaporation from single Cu$_x$S source, as an alternative to the chemiplating technique for fabricating Cu$_x$S layer in Cu$_x$S/CdS solar cells. Deposition rate less than 150 Å/min produced Cu$_x$S layers with chalcocite as major phase. Layers free from excess copper have chalcocite-related phase transition between 75 and 80 °C. Also they exhibited room temperature resistivity between 10$^{-2}$ and 10$^{-3}$ Ω.cm. and showed direct and indirect band gaps of 2.25 and 1.25 eV respectively. For solar cell fabrication Cu$_2$S layer with well controlled evaporation conditions was deposited on hot CdS thin film substrates [161].

Low cost Cu$_2$S/CdS thin film solar cells having efficiency of 4.5 % were also prepared through chemical spraying. For solar cell fabrication thin transparent tin oxide transparent electrode was sprayed over glass substrate. Over this CdS layer was spray deposited. A very thin film of Cu$_x$S was then formed by spraying, dipping, or electrolytic ion exchange. Finally for top
contact copper/lead electrode was evaporated over the Cu₅S layer [162]. Islam et al. prepared thin film CdS/Cu₂S heterojunction solar cells on gold grid plated glass substrates by first depositing Cu₂S employing elemental evaporation of copper and sulphur and then evaporating CdS. Here the cells were prepared with Cu₂S layer sandwiched between the glass substrate and the CdS layer and was found to be stable. The maximum efficiency was 5 % for these solar cells [163].

Vanhoecke prepared Cu₂S/CdS solar cell by sputtering thin chalcocite (Cu₂S) films using pure copper target in an H₂S-Ar atmosphere onto evaporated CdS layer. For active area of 3.6 cm², efficiency of up to 4.9 % was attained. On large area cells (21cm²) efficiency of 2.4 % was attained. They were able to reduce the thickness of CdS layers to 10 μm for obtaining good quality solar cells [164]. Wu et al. prepared colloidal Cu₂S nanocrystals by injection reaction between copper (II) acetylacetonate and ammonium diethyl dithiocarbamate in mixed solvent of dodecanethiol and oleic acid. Cu₂S nanocrystal was used as active light absorbing component in combination with CdS nanorods to make solution-processed solar cell with 1.6 % power conversion efficiency on both conventional glass substrates and flexible plastic substrates. The device showed stability over 4 month testing period [165].

1.10 Significance of the present work

For thin film preparation, present study followed simple, cost effective and versatile CSP method. As cost effectiveness is the primary necessity prevailing in photovoltaic industry, CSP method is a suitable candidate capable of fulfilling this demand. Moreover, feasibility of large area deposition offers special recognition for CSP among industrially viable thin film solar cell techniques. CuInS₂ and Cu₂S are the absorber materials for the present study.
Optical absorption coefficients and band gaps of these materials are ideal as an absorber in thin film solar cells. Comparing with CdTe and CuInSe₂, these materials are non-toxic, earth-abundant and simple CSP method can be effectively used to deposit device quality films using these two materials. Buffer layer used for the present study is In₂S₃, which is also non-toxic when comparing with CdS buffer layer. Spray pyrolysed In₂S₃ is a well-studied and proven buffer layer for solar cell application. The main issue that limits the performance of solar cells based on thick absorber layer is the reduced collection probability of light generated carriers at the contacts due to recombination in thick absorber layer. In this context, the concept of ETA solar cell was also introduced for both CuInS₂ and Cu₂S based solar cells. The main idea was to reduce the thickness of the absorber layer in which light-generated electron-hole pairs travel to reach the electrical contacts before recombining. As the absorber layer thickness was reduced, light absorption will reduce considerably. In order to compensate this, multiple band gaps of CuInS₂ and Cu₂S was introduced by CSP in this extremely thin absorber layer so that device can absorb photons of two different energies.
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Chapter 1


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