CHAPTER-I
Introduction and Theoretical Background
1.1. Introduction:

The economic growth in many parts of the world during the past decade was able to be sustained because of the affordable energy prices. The worldwide energy utilization has increased every year by several percentages [1]. Due to an overall growth of world population, it is believed that this growth will persist or even accelerate over the coming decades [2,3]. About 13 terawatts (TW) of energy is currently needed to sustain the lifestyle of 6.5 billion people worldwide. By year 2050, we will need an additional 10 TW of clean energy to maintain the current lifestyle. Most of this energy is nowadays supplied by fossil fuels and/or nuclear energy. However, these resources are limited and their use has a serious environmental impact, which extends probably over several future generations [4]. This situation poses an enormous challenge already for the present generation to start up a transition in energy consumption and production. More efficient usage of produced energy could possibly lead to a decreased consumption whereas new technologies could steer this transition towards a more sustainable energy production.

Sustainable development meets the needs of today without jeopardizing the future. In this respect, renewable energy sources fit in very well. Besides their environmental friendliness, they offer several other advantages [5, 6]. Diversification of energy supplies can lead to more economical and political stability. Moreover, countries and regions can become more independent by supplying their own energy from renewable instead of having to import fuels or electricity from large production plants. Finally, a transition from traditional fuel based energy production to renewable energy resources can even lead to a substantial increase of employment.

Several renewable energy sources are under development or even
already introduced on the market. Still, they make up only a limited part of the
total energy production [7]. At this moment, energy produced from biomass –
termed bioenergy accords the largest share of renewable energy. This type of
energy supply has important benefits. Bioenergy is carbon neutral and
therefore does not contribute to the greenhouse effect. Furthermore, biomass
can be regarded as a means to store solar energy by photosynthetic
conversion. This solar power can afterwards be released continuously by
combustion of the natural materials and thus create a base-load electricity.

Another renewable energy source that can serve as base load
resource in electrical networks is geothermal energy. The earth’s heat
becomes available to us by e.g. natural hot springs and can be used as such
or converted into electricity. However limited in access, geo-thermal energy is
a huge resource that is already exploited to a growing extend.

Other renewable energy sources that are available to us are water and
wind energy, which however could also be regarded as originating from solar
energy. Hydro electricity is already widely exploited and according to some
predictions the growth of this energy source will be limited in the near future.
Wind energy on the contrary is only scarcely used up to now and is therefore
still far below it’s full potential as renewable energy source.

The direct use of solar energy as renewable and sustainable resource
is also believed to have much larger possible applications than used
nowadays. The total amount of solar irradiation per year on the earth’s
surface equals 10000 times the world’s yearly energy need. This solar power
can on the one hand be applied passively as lighting resource and space
eating in buildings. Besides this, active applications concern the heating of
water or heat fluids through concentrator systems for domestic use or even in
industrial processes. The photovoltaic (PV) conversion of light directly into
electricity is another possible way to make use of solar energy [8]. Especially
for this latter kind of application widespread use is possible and even foreseen
due to several reasons:

- It is environmentally benign, with no emission during operation
- It converts light directly into electricity
- It requires little maintenance and is very reliable
- It is the largest non-carbon-based energy source (100,000 TW)
It is modular and therefore can serve small as well as very large power demands

In conclusion, it can be stated that photovoltaic conversion of solar energy directly into usable electricity has large potential as a renewable and sustainable energy supply for the future. It will offer substantial environmental as well as economical benefits to both developed and developing countries. At present an annual growth rate of more than 30% of the PV market is seen. Despite such an impressive number, it will take still more than 30 years to get a significant contribution by photovoltaic energy supply to the total world energy demand. Novel device concepts and materials might offer solutions, however still much basic research and development is necessary in several of these areas. Also organic materials based photovoltaic devices are intensively studied in this respect. An overview of activities in this field will be given further on. First, a basic and general description of solar cells is put forward and the most relevant parameters are explained.

1.1.1 Introduction of Solar cell:

A solar cell is a device that converts the energy of sunlight directly into electricity by the photovoltaic effect. Sometimes the term solar cell is reserved for devices intended specifically to capture energy from sunlight such as solar panels and solar cells, while the term photovoltaic cell is used when the light source is unspecified. Photovoltaic is the field of technology and research related to the application of solar cells in producing electricity for practical use. The energy generated this way is an example of solar energy.

The word ‘photovoltaic’ comes from the Greek word *phos* which stands for light and *voltaic* for the electrical potential. This latter volta refers to the researcher Alessandro Volta (1745-1827), who was one of the pioneers in the study of electricity. Therefore, the word expresses in itself already that a photovoltaic device is able to convert light into electricity. Photovoltaic effect was first recognized in 1839 by French physicists A.E. Becquerel. In 1883, the first solar cell was built by Charles Fritts. He coated selenium with extremely thin layer of gold to form the junction. Since the discovery of a p–n junction Si photovoltaic (PV) device reported in 1954, the science and technology of PV devices (solar cells) and systems have undergone revolutionary
The working principle of solar cell is illustrate in the fig. 1.1

![Working principle of photovoltaic/solar cell](image)

Conventional solar cells are made up of semiconducting material, usually silicon. When light hits the cells, they absorb energy though photons. This absorbed energy knocks out electrons in the silicon, allowing them to flow. Additionally it creates electron-hole pair (EHP). By adding different impurities to the silicon such as phosphorus or boron, an electric field can be established. This electric field acts as a diode, because it only allows electrons to flow in one direction. Consequently, the end result is a current of electrons, better known to us as electricity.

### 1.1.2 Generations of Solar cells:

There are three basic generations of solar cells, though one of them doesn't quite exist yet, and research into it is ongoing.

First generation solar cells are dominant technology in commercial production, accounting more than 85% of solar cell market. These solar cells are manufactured in a fashion similar to computers, involving extremely pure silicon. They are very efficient, approaching their theoretical efficiency maximum of 33%. The manufacturing processes that are used to produce first generation cells are inherently expensive, meaning that these cells may take years to pay for their purchasing costs. It is not thought that first generation cells will be able to provide energy more cost effective than fossil fuel sources. The first generation of solar cells has high-cost, high-efficiency.
The second generation of solar cells, which have been under intense development for the 90s and early 2000s, are low-cost, low-efficiency cells. These are most frequently associated with thin film solar cells, designs that use minimal materials and cheap manufacturing processes. The most popular materials used for second generation solar cells are copper indium gallium selenide, cadmium telluride (CdTe), amorphous silicon and micromorphous silicon. Though these cells have only 10-15% conversion efficiency, the decreased cost makes up for this shortfall and it is thought that second generation solar cells will surpass first generation cells in market share sometime around 2015. Second generation solar cells have the potential to be more cost effective than fossil fuel, though this may not occur until 2015 or later.

Second generation materials have been developed to address energy requirements and production costs of first generation cells. Alternative manufacturing techniques such as vapour deposition, electroplating, chemical bath deposition are advantageous as they reduce high temperature processing significantly. It is commonly accepted that as manufacturing techniques evolve production costs will be dominated by constituent material requirements, whether this be a silicon substrate, or glass cover.

Third generation solar cells are just a research target, and do not really commercially exist yet. The goal of third generation solar cell research is low-cost, high efficiency cells. Third generation technologies aim to enhance poor electrical performance of second generation (thin-film technologies) while maintaining very low production costs. Current research is targeting conversion efficiencies of 30-60% while retaining low cost materials and manufacturing techniques. Some analysts predict that third generation cells could start to be commercialized sometime around 2020, but this is just a guess. Technologies associated with third generation solar cells include multi junction photovoltaic cells, tandem cells and nanostructured cells to better pick up incident light, and using excess thermal generation to enhance voltages or carrier collection. The most popular devices used for third generation solar cells are photoelectrochemical solar cells, dye sensitized solar cells-Graetzel cells, quantum dot sensitized solar cells, polymer solar cells, etc.
Third generation solar cells can exceed the theoretical solar conversion efficiency limit for a single energy threshold material. The threshold was calculated in 1961 by Shockley and Queisser as 31% under 1 sun illumination and 40.8% under maximal concentration of sunlight (46,200 suns, which makes the latter limit more difficult to approach than the former).

The best result cell efficiency of the first to third generations are collectively represented in fig 1.2

![Best Research Cell Efficiencies](image)

**Fig. (1.2) Cell efficiencies of first to third generation solar cells**

1.1.3 Characteristics of Solar cells:

A photovoltaic cell may be represented by the equivalent circuit model shown in figure (1.3). This model consists of current due to optical generation ($I_L$), a diode that generates a current [$I_S(e^{qV/KT})$], a series resistance ($r_s$), and shunt resistance ($r_{sh}$). The series resistance is due to the resistance of the metal contacts, ohmic losses in the front surface of the cell, impurity concentrations, and junction depth. The series resistance is an important parameter because it reduces both the short-circuit current and the maximum power output of the cell. Ideally, the series resistance should be 0Ω ($r_s = 0$). The shunt resistance represents the loss due to surface leakage along the edge of the cell or due to crystal defects. Ideally, the shunt resistance should
be infinite \( r_{sh} = \infty \)

![Equivalent circuit and schematic symbol of solar cell](image)

**Fig. (1.3) Equivalent circuit and schematic symbol of solar cell**

If a load resistor \( R_L \) is connected to an illuminated PV cell, then the total current becomes:

\[
I = I_S(e^{\frac{qV}{kT}} - 1) - I_L \tag{1.1}
\]

where, \( I_S = \) current due to diode saturation

\( I_L = \) current due to optical generation

Several factors determine the efficiency of the solar cell, including the maximum power point \( P_{max} \), the energy conversion efficiency \( \eta \), and the fill factor \( FF \). These points are illustrated in figure (1.4), which shows a typical forward bias I-V curve of an illuminated PV cell. The maximum power point \( P_{max} \) is the product of the maximum cell current \( I_{max} \) and voltage \( V_{max} \) where the power output of the cell is greatest. This point is located at the “knee” of the curve.

![Typical forward bias I-V characteristics of a PV cell](image)

**Fig. (1.4) Typical forward bias I-V characteristics of a PV cell**

The fill factor is a measure of how far the I-V characteristics of an actual PV cell differ from those of an ideal cell. The fill factor is defined as:

\[
FF = \frac{I_{max}V_{max}}{I_SV_{oc}} \tag{1.2}
\]

where, \( I_{max} = \) the current at the maximum power output
\[ V_{\text{max}} = \text{the voltage at the maximum power output} \]
\[ I_{\text{sc}} = \text{the short-circuit current} \]
\[ V_{\text{oc}} = \text{the open-circuit voltage} \]

Another important parameter is the conversion efficiency (\( \eta \)), which is defined as the ratio of the maximum power output to the power input to the cell:

\[
\eta = \frac{P_{\text{max}}}{P_{\text{in}}} \quad \text{---------------------------------------- (1.3)}
\]

\[
FF = \frac{P_{\text{m}}}{V_{\text{oc}} \times I_{\text{sc}}} = \frac{\eta \times A_e \times E}{V_{\text{oc}} \times I_{\text{sc}}} \quad \text{---------------------------------------- (1.4)}
\]

where, \( P_{\text{max}} \) = the maximum power output
\( P_{\text{in}} \) = the power input to the cell

These described parameters of the solar cell can be determined through electrical characterization of the device.

**1.1.4 Photoelectrochemical (PEC) solar cell:**

Much effort has been directed towards developing new and better solar energy conversion and storage devices. In the 1970s, a strategy was suggested in which a solid-liquid junction was used. Here, instead of the solid-solid junction of conventional solar cells, a semiconductor electrode dipped in a liquid electrolyte provided the necessary charge transfer, a redox ionic species being used to obtain photovoltage/photocurrent. In 1972 Fujishima and Honda used such an approach to photoelectrolyse water and thus obtained hydrogen; in 1975, Gerischer succeeded in the direct conversion of solar energy into electricity, a strategy that offers the possibility of both solar energy conversion and storage: photoelectrochemical solar cells.

During the last decade much work has been done on photoelectrochemical (PEC) system [9] in search of suitable liquid junction photovoltaic solar cells. One of the advantages is that the photoelectrochemical cell offers a good electrical contact for solar energy applications. That is formed as soon as the semiconductor electrode is immersed in the electrolyte. Another one is that, with a proper choice of redox couple in the electrolyte, the Fermi level in the electrolyte can be controlled.
and thus the barrier height can be adjusted to the desired level. The good contact formed at the electrode / electrolyte interface makes it feasible to use the cheap polycrystalline materials.

Thus, PEC solar cells can in principle be much cheaper than the traditional solid state cells. This is particularly important because of the comparatively low solar radiation power density requiring the use of large area converters. The future prospects of photoelectrochemical solar energy conversion method depend on how completely its potential advantage can be realized in practice. Secondly, the photoelectrochemical method is convenient in that one of its versions - photoelectrolysis, enables light energy to be directly converted into chemical energy of the photoelectrochemical reaction products, and thus permits the energy storage problem to be solved along with proper energy conversion.

Cadmium chalcogenides are among the most studied materials as photoelectrode in photoelectrochemical cells [10]. Interest in such PEC system is that, in aqueous polysulphide or polyiodide solutions, a drastic decrease in photo corrosion is observed as compared to other aqueous solutions, while reasonable conversion efficiencies can be obtained. An important consideration from the practical point of view is that thin film polycrystalline photoelectrode can be prepared by various methods with conversion efficiencies of more than half of those obtained with single crystal based PEC’s [11].

**Basic electrochemistry:**

1. **Oxidation and reduction Process**

   A process in which substance gains an electron is called a reduction reaction [12].

   \[ \text{OX} + e^- \leftrightarrow \text{Red} \quad E^0 \]  

   where, OX and Red are oxidized and reduced species and \( E^0 \) is the standard electrochemical potential. The reverse process of losing an electron is called an oxidation reaction. In a system, where one species loses an electron and other species gains an electron is called redox system. If \( E^0 \) is
positive, the reaction proceeds from left to right and when it is negative, the reaction proceeds from right to left.

Gerischer, while deriving an analogy with semiconductor physics, has suggested that the oxidized and reduced species may be linked with the conduction and valence band respectively [13]. A term similar to Fermi level $E_F$ of a semiconductor can be defined for redox couple also and can be abbreviated as $E_{\text{fredox}}$. The energy necessary to transfer an electron from reduced species to the oxidized species is analogous to the bandgap of a semiconductor. The redox potential is defined as the potential required to transfer an electron from redox to the vacuum level or vice-versa [14].

**ii. Semiconductor-electrolyte Interface**

Photoelectrochemical process can be both, photoelectrical and photoelectrochemical in nature. When semiconductor is dipped in redox solution, as its chemical potential is different from the redox potential ($E_{\text{redox}}$), a new equilibrium is established between the semiconductor and electrolyte solution by rearrangement of charges. This results in a strong field near the junction. When the semiconductor-electrolyte junction is illuminated with light having energy greater than the bandgap energy of semiconductor, electron-hole pairs are produced in the depletion layer. Charge separation takes place due to the local field present at the interface. The probability of annihilation of a hole with an electron is reduced by this field. This condition will be optimum when the light penetration depth is equal to the depletion layer width. So that all the light is absorbed in the depletion layer and maximum number of electron-hole pairs are produced in it. These separated charges produce a counter charge and under open circuit conduction this counter field is maximum. This is the open circuit voltage. The conduction band and valance band get shifted due to the counter voltage. The photovoltage is given by the change in the Fermi level as shown in Figure (1.5). When a counter electrode is immersed in the electrolyte and connected externally to the semiconductor, the photo generated electron moves into the bulk of semiconductor through the external circuit; it reaches the counter electrode to reduce an oxidized species in the electrolyte. The hole is pushed to the electrode surface where it oxidizes a species in the electrolyte. The photocurrent depends on the
absorption coefficient of the semiconductor, width of the space charge region, hole diffusion length, area of illuminated electrode, photon energy and radiation intensity. Under short circuit conditions, the Fermi levels of the semiconductor and the potential of the redox couple of the solution are equalized and a net charge flows during the illumination.

**Fig. (1.5) The position of bands under illumination responsible for photo induced charge transfer**

**Classification of the PEC solar cells**

The principle of charge transfer reaction at the semiconductor-electrolyte interface forms the basis of various types of PEC cells. In addition to the semiconductor-electrolyte interface, incorporation of a counter electrode in the electrolyte to complete the electrical circuit gives the desired photoelectrochemical cell. The various types of PEC cells can be categorized according to the net free energy change ($\Delta G$) in the overall system as given below.

**a. Electrochemical photovoltaic cells ($\Delta G = 0$)**

It consists effectively of such a redox couple that the total cathodic and anodic reactions do not lead to net chemical change. The electrodes do not participate in the chemical reaction, they only serve as a “shuttle” for the charge transfer mechanism. At the semiconductor electrode,

$$\text{(Red)}_{\text{solv.}} + h^+ \leftrightarrow \text{(OX)}_{\text{solv.}} \tag{1.6}$$
At the metal counter electrode,

\[(\text{OX})_{\text{solv.}} + e^- \leftrightarrow (\text{Red})_{\text{solv}}\]  

(1.7)

The above cell is the regenerative type PEC cell used for direct production of electricity.

**b. Photoelectrolysis cells \(\Delta G > 0\)**

Effectively two redox couples are present and a net chemical change takes place in the system. The photoelectrolysis cells and some electrochemical storage cells belong to this category. Some examples of reaction for the above type are

\[\text{H}_2\text{O} \xrightarrow{h\nu} \text{H}_2 + \frac{1}{2}\text{O}_2\]  

(1.8)

\[\text{CO}_2 + \text{H}_2\text{O} \xrightarrow{h\nu} \text{CH}_2\text{O} + \text{O}_2\]  

(1.9)

Hence, optical energy is converted in to chemical energy.'

**c. Photocatalytic cells \(\Delta G < 0\)**

In these cells also such redox couples are present that net chemical changes take place. Hence \(\Delta G < 0\) and the optical energy provide the activation energy for the chemical reaction. Example for photocatalytic cell is

\[\text{N}_2 + 3\text{H}_2 \xrightarrow{h\nu} 2\text{NH}_3\]  

(1.10)

The category (b) and (c) are some times termed photoelectrosynthetic cells.

**Construction of PEC solar cell**

A PEC solar cell is defined as an electrochemical cell in which one or both electrodes are semiconductors such that irradiation of the semiconductor
results in the non-spontaneous flow of current in the external circuit. Such cell is distinct from a photogalvanic cell, in which light absorption occurs in the solution and not in the electrode. An PEC cell consists of a semiconductor photoelectrode, an electrolyte and a counter electrode as shown in Figure (1.6a). All parts play an important role in the PEC cell. The distance between photoelectrode and counter electrode is 0.4 cm. When both the electrodes are immersed in the electrolyte, the band bending of the semiconductor photoelectrode may occur. The transfer of electrons to or from the electrolyte can take place only in the energy region of the conduction band, while the hole transfer can take place in the region of the valance band. Such a transfer can occur between two states of the same energy, one empty and other filled. When the interface of the semiconductor photoelectrode-electrolyte is illuminated, the electron-hole pairs are generated in the depletion layer and are separated by the electric field present at the interface. The incident energy of photon should be greater than the bandgap energy of the semiconductor. The electron-hole pairs generated in the bulk of the semiconductor are essentially lost through recombination. If a positive potential is applied to the n-type semiconductor photoelectrode and illuminated, the electron-hole pairs are generated and the separated electrons rise to the top of the conduction band and holes in the valence band. This process sets up a counter field under open circuit conditions. The counter field is at its maximum and is the open circuit voltage; \( V_{oc} \) is given by the equation:

\[
V_{oc} = \frac{nKT}{e} \log \left[ \frac{I_{sc} + 1/I_0}{1} \right] \]  

(1.11)

On the other hand, the counter electrode is being in the same electrolyte, the photo voltage acts as a driving force for the electrons to move under the short-circuit conditions from the semiconductor electrode to the counter electrode and a regenerative cell is formed and is shown in Fig.(1.6b). The short-circuit current is given by the equation:

\[
I_{sc} = I_0 \left[ \exp \left( \frac{eV_{oc}}{nKT} \right) - 1 \right] \]  

(1.12)

The electrons promoted to the conduction band drift towards the interior, while the holes, the minority carriers, come to the surface of the semiconductor.
Here they encounter the reduced form of the redox couple in the solution. The component is oxidized by the holes, transported to the counter electrode and therefore gets reduced. This reduction is driven by the external connection from the semiconductor.

![Diagram](image)

**Fig. 1.6** (a) - A typical electrochemical photovoltaic cell and (b) - Current flow and energy level diagram for n- semiconductor PEC cell

**Requirements of PEC cells**

Following are the requirements, expected for achieving good performance of the PEC cell

1. **Semiconductor photoelectrode**
   
   The semiconductor photoelectrode is the heart of the PEC cell. The property of a semiconductor photoelectrode reflects the changes in the electrical properties of a cell. Semiconductor photoelectrode used in PEC cell for the achievement of good performance should satisfy the following requirements:

   1. The bandgap (Eg) of the photoelectrode materials should match with the maximum span of the solar spectrum i.e. 1.4 to 1.6 eV.
   2. It should remain stable in the dark as well as under illumination.
   3. It should be of the direct bandgap type with high optical absorption coefficient
   4. Charge carriers in the material should have high mobility and life time.
   5. Thickness should be large enough to absorb all the incident radiation.
   6. Cost of manufacturing and efficiency should be accepted.
7. Diffusion length of minority carriers should be as large as possible.
8. Series resistance $R_s$ should as small as possible and shunt resistance $R_{sh}$ should be large enough, ideally $R_s = 0$ and $R_{sh} = \infty$.

ii. Electrolyte

An important parameter in the PEC cell is the electrolyte. Electrolytes consist of the oxidized species and the reduced species. These species are ionic species which helps to transfer the photo generated holes from photoelectrode to the counter electrode.

The energy levels in the electrolyte are analogous to the concept of energy states in the solid and $E_{F,\text{redox}}$ is equivalent to the Fermi energy of the semiconductor. If the semiconductor electrode is brought in contact with the redox electrolyte, the equilibrium situation is achieved by the electron exchange at the surface, the Fermi level of the semiconductor adjusts with each other. This produces a barrier height which depends on the nature of the solution species and particular semiconductor. It is observed that aqueous electrolytes cause surface modification and restricts the use of many semiconductors. Molecular inorganic solvents with supporting electrolytes and mixtures of totally ionic molten salts have submitted for aqueous electrolytes Requirements of electrolytes for the PEC cells:

1. Reduction-oxidation reactions should occur appropriate to the semiconductor band edges.
2. Charge transfer rates of oxidized and reduced species at both semiconductor and counter electrode should be high or effective.
3. Oxidized, reduced species and solvent components should have photo and thermal stability through useable solar spectrum and operational temperature range.
4. Oxidized, reduced species and supporting electrolyte concentration in solvent should be adequate to reach required current densities.
5. The electrolyte should have minimum optical absorption.
6. It should be non-corrosive to electrodes.
7. Ionic conductance of electrolyte should permit negligible ohmic losses.
8. Toxicity, reactivity and cost should preferably below.
iii. The Counter electrode

The counter electrode is important, it must satisfy regenerative processes, the electrolyte species are oxidized at the counter electrodes giving no net chemical change in the composition of electrolyte. The requirements for the counter electrode for better performance in the PEC cell are:

1. The counter electrode should not react with electrolyte. i.e. it should be chemically inert.
2. It must be electronically active i.e. the charge transfer between the counter electrode and redox species in the electrolyte must be fast.
3. The area should be large to avoid concentration polarization.
4. When a counter electrode is immersed into the electrolyte, the half cell potential of the electrode should match with that of the half cell potential of the semiconductor electrode.
5. The counter electrode should have a low potential for the reduction reaction.
6. The counter electrode must be cheaper; platinum and graphite are the most commonly used. Graphite electrode acts as a catalytic reagent and gives better performance than the Pt, Ag₂S and Au in the aqueous electrolyte.

1.2 Survey of Literature:

1.2.1 Survey of literature on CdS:

Metal chalcogenides (sulphides, selenides and tellurides) have been studied intensively over the past 60 years in view of their actual and potential applications as photoconductive cells, photovoltaic cells and other optical devices. The metal chalcogenide thin films, such as those of CdS, are one important example of film SC electrodes. CdS nanocrystalline thin films belonging to the cadmium chalcogenide family and used as window material for CdS/CdTe solar cells continues as a subject of intense research due to its potential application in solar cells [15 – 19].
Structural Properties of CdS

Cadmium sulfide is a chemical compound with the formula CdS. It is yellow in color and is a direct band gap semiconductor, with a bandgap of 2.42 eV at 300 K. Cadmium sulfide has, like zinc sulfide, two crystal forms; the more stable hexagonal wurtzite structure (found in the mineral Greenockite) and the cubic zinc blende structure (found in the mineral Hawleyite) shown in fig. (1.7). In both of these forms the cadmium and sulfur atoms are four coordinate [20-24]. The chemical bonding of both phases is commonly described by sp\(^3\) hybridization. In both structures, the coordination shell of the anion is made up of four cations in tetrahedral symmetry and the second neighboring shell is made up of 12 anions. One can look on these structures as having closely packed ions of S with Cd ions in tetrahedral voids.

![Crystal structures of CdS](image)

**Figure (1.7)** Crystal structures of CdS (a)-cubic, (b)-hexagonal

CdS is one of the important material for application in electro-optic devices such as laser materials, transducers, photoconducting cells, photosensors, optical wave-guides and non-linear integrated optical devices [25] electrochemical cells, gas sensor [26] Recently, CdS is also applied to dye-sensitized photoelectrochemical cells to improve their performance [27,28]etc.
Literature survey of chemical bath deposited CdS thin films

Several techniques have been used to fabricate CdS thin films, such as electrodeposition, chemical bath deposition (CBD), screen printing (SP) and physical vapour deposition. Today, there has been a prevailing need for efficient, low temperature and low-cost deposition methods of material preparations for thin films as technological industrial applications. Chemical bath deposition (CBD) is a soft solution process that is capable of producing high-quality thin film at relatively low temperature. The fundamental CBD growth mechanism is similar to that of chemical vapor deposition (CVD), involving mass transport of reactants, adsorption, surface diffusion, reaction, nucleation and growth. Chemical bath deposition provides a simple and low-cost method to produce uniform, adherent and reproducible large-area thin films for thin-film electronics applications such as solar cells [29]. Historically, the first application of CBD was reported by Reynolds [30] for the fabrication of lead sulfide photoconductive detectors in 1884. The reaction proceeded in a basic solution and a strongly adherent layer was formed on the interior surfaces of the reaction vessel. The first general review for CBD was reported by Chopra [31] in 1982. Several years later, a review by Lokhande [32] was published with an emphasis on the deposition of metal chalcogenides. A comprehensive review was reported by Lincot [33] in 1998, with a detailed analysis on the growth kinetics. Two more reviews by Nair [34] and Savadogo [35] reported on their extensive work in the field with an emphasis on solar energy-related issues. Regardless of the deposition technique, the characterization of the post-deposited films and optimization of the deposition processes are still open subjects for research. A large number of studies have been carried out to achieve this goal in order to produce CdS thin films with good optoelectronic properties suitable for photovoltaic applications.

Fifty years ago, Mokrushin et al. and Kitaev et.al reported the potential application of CdS [36,37]. Kaur et.al and Pandya et al. reported the CdS as a window layer in CIGS cells [38,39]. For window layer in heterojunctions solar cells, the thin film must possesses high optical throughput with minimal resistive loss, the band gap of the window layer should be as high as possible and thickness as thin as possible to maintain low series resistance. Many
researcher attempts for high band gap and low thickness of CdS thin film preparation by wet chemical method. Moutinho HR and co-workers were deposited CdS thin film by close-spaced sublimation (CSS) and chemical bath deposition (CBD), in order to investigate why the best PV devices were obtained using CBD CdS. It was found that one of the reasons for the best performance of the CBD CdS was that, unlike the CSS CdS, these films grew conformal on the underlying SnO$_2$ film, which was used as a front contact. The conformal growth promotes a film with a more uniform thickness, minimizing shunting paths [40]. K.L.Chopra reported in the survey on thin film solar cell that the CIGS solar cells based on superstrate structure is inferior to substrate structure because of the inter-diffusion of CdS during high temperature CIGS film growth. Using same terminology, Ramanathan et al. reported about 19 % efficiency of CIGS with CdS buffer layer [41].

The band gap of semiconductor is found to increases due to a decrease in the particle size; this is known as the quantum size effect. For the window layer in solar cells, size quantized CdS thin films are applied. Louis Brus critically review, and discuss in greater detail, his team reported experimental and theoretical work in the size-dependent development of bulk electronic properties in semiconductor crystallites of about15 to several hundred angstroms [42]. Nozik and co-workers [43] report initial experiments with small colloidal particles of CdS (<50 Å) that show optical effects due to quantization in three dimensions. For the preparation of CdS colloids in water with particle diameters (<50 Å), 24 mL of 3.65 mM Cd(ClO$_4$)$_2$ containing 1 mM (NaPO$_3$)$_6$ (colloid stabilizer) and 21% methanol was cooled to 273K for 2 h. Then, 1 mL of 4.4 mM Na$_2$S was injected by a syringe, without mixing, into the cold cadmium solution. The resulting colloid was filtered through a membrane ultra filter with a pore size of 50 Å and the particle diameter was 30-40 nm. Torimoto et al. [44] reported electro chemical atomic layer epitaxy (ECALE) method for size quantized CdS thin film for photoelectrochemical application. They mention that, the results are not expected at all if size quantization effects were operative in the CdS film electrodes, because negative shifts in the potential of the conduction band edge are expected in that case. It was observed that cathodic currents
Chapter-I Introduction and Theoretical Background

commenced to flow at around 1.3V vs Ag/AgCl in the dark and became great with increasing cathodic polarization of the electrode. Considering this finding, the currents seem to result from either hydrogen evolution or cathodic corrosion of CdS, and superimposition of the cathodic currents on the anodic photocurrents makes the size-quantization effects uncertain. Vossmeyer et al. [45] reported improved synthetic routes for the preparation of almost mono-disperse CdS clusters. Six samples of 1-thioglycerol stabilized clusters with diameters of approximately 13, 14, 16, 19, 23, and 39 Å have been prepared as fully redispersible powders. K.K. Nanda et al. [46] prepared CdS of different crystalline size over metal/glass substrates by a precipitation technique using precursors as CdSO₄, thiourea and NH₄OH. The different crystalline sizes were obtained by controlling the reaction time period/thickness, temperature and pH of the solution. Nanocrystalline CdS showing quantum size effect were prepared at 300 K having solution pH=11.7. The samples are then subjected to different characterizations. A blue shift of 0.74 eV has been achieved in the present case due to quantum size effect in CdS nanoparticles.

Hodes and co-workers [47-50] reported size quantization of CdS by CBD and electrodeposition. They studied the role of Cd(OH)₂ in the formation of CdS films. Hodes reported that, size-quantized CdS ~ 4 to 5 nm cross-section by 15 nm height as a buffer layer on CuInS₂. The resulting CuInS₂/CdS thin-film solar cells gave increased photocurrents and higher light-to-electricity conversion efficiencies ~11% than those made with conventional non quantized CdS films. This was due mainly to the increased bandgap of the quantized CdS, allowing more light to reach the active CuInS₂ layer. Yao and co-workers [51] reported fabrication and photoelectrochemical characterization of CdS particles in nanospaces of expandable mica. Jinesh and co-workes [52] investigate how quantum confinement comes in chemically deposited CdS. They use XPS spectra for the investigation. Jinesh et al. reported that, the increase in Cd(OH)₂ in the sample with the increase of the pH of the bath, observed in XPS depth profile, depicts the possibilities that the CdS clusters of finite size are embedded in Cd(OH)₂ surroundings, which
ultimately makes the clusters electrically isolated and hence provides carrier confinement.

The use of polymers is a prominent method for the synthesis of semiconductor nanoparticles. The reason is that the polymer matrices offer advantages like easy processability, solubility and control of the growth and morphology of the nanoparticles. CdS nanoparticles embedded in different matrixes like polystyrene, polyvinyl alcohol, polyethylene glycol etc. have been prepared by many workers [53-58]. Hwang and co-workers [59] reported CdS nanoparticles on the surface of single walled carbon nanotubes (SWNTs). Z. Qian and co-workers [60] reported CdS-PAMAM composite nanocrystalline thin film useful for photoelectrochemical sensors.

Photoelectrochemical performance of CdS thin films are enhanced by increasing surface area or by post deposition treatment. Pandey and co-workers and Tiwari [61, 62] reported that, the due to surface treatment polycrystalline CdS thin films show good photoelectrochemical behavior in a polysulphide electrolyte with high conversion efficiency and stability.

<table>
<thead>
<tr>
<th>SC electrode</th>
<th>Monocrystal or Film</th>
<th>Counter Electrode</th>
<th>Electrolyte</th>
<th>Redox Couple</th>
<th>Efficiency (η)</th>
<th>Stability</th>
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<tr>
<td>CdS (E_g=2.4eV) M</td>
<td>MnO2</td>
<td>KCl-K2Fe(CN)6-K3Fe(CN)6</td>
<td>Fe(CN)6^3-&gt;</td>
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<tr>
<td>M</td>
<td>C</td>
<td>KOH+Na2S</td>
<td>S^2-&gt; S^2-</td>
<td>1.0</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>Pt</td>
<td>KCl</td>
<td>CH3OH</td>
<td>-</td>
<td>5.0</td>
<td>Unstable</td>
</tr>
<tr>
<td>M</td>
<td>Pt</td>
<td>KCl+hydroquinone</td>
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<td>-</td>
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<tr>
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<td>Pt</td>
<td>NaOH+Na2S</td>
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<td>S^2-&gt; S^2-</td>
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<td>MnO2 glass of Au</td>
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<tr>
<td>F</td>
<td>Pt</td>
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<td>S^2-&gt; S^2-</td>
<td>0.9</td>
<td>Stable</td>
<td></td>
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</tbody>
</table>

Table (1): Efficiency of PEC of CdS photoelectrode
Jadhav et al. [63] reported the effect of Cd:S ratio on the photoconducting properties of CdS films. CdS films have been chemically deposited with different Cd:S ratios. Their electrical and structural properties have been studied. The photoconducting studies of such films showed that the photoconductivity has been improved with Cd:S ratio as 1:0.2. Patil et.al [64] reported the enhancement in PEC performance due to effect of complexing agents. The air annealed CdS thin film with triethanolamine (TEA) and ammonia as complexing agents shows the better short circuit current. Hillal and co-workers [65] reported the PEC performance of CdS thin film prepared by CBD can be significantly enhanced by pre-annealing the electrode at 250°C followed by its slow cooling. Chaure and co-workers [66] investigated electronic quality of chemical bath deposited CdS layers for photovoltaic solar cells. A typical bath contains 0.02 M CdCl₂, 0.07 M NH₄Cl and 0.14 M thiourea. The P哙 of the bath is maintained at 9.5 and the temperature is kept at 90°C. After the deposition of 15 min the film thickness is found to be 0.1–0.2 µm. Dongre and co-workers [67-68] synthesized flower-like CdS nanostructured films and they studied their application in photoelectrochemical solar cells. The films of CdS have been grown over metal/glass substrates by a CBD technique using precursors as CdSO₄, thiourea and NH₄OH. They found that the flower like morphology enhances the PEC properties as compare to planer morphology. In another report Dongre et al. reported nanowires like morphology of CdS thin films but with fewer short circuits current. This report explains that, the morphology with complex nanostructures is potentially even more interesting for the applications of solar energy harvesting and conversion. Table (1) is showing the efficiency of PEC of CdS photoelectrode [69]

1.2.2 Survey of literature on ZnO:
Most of the group-II-VI binary compound semiconductors crystallize in either cubic zinc-blende or hexagonal wurtzite structure where each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa.
Structural Properties of ZnO

Zinc Oxide is a chemical compound with the formula ZnO. It is white in color and is a direct band gap semiconductor, with a bandgap of 3.2 eV at 300 K. The crystal structures of ZnO are wurtzite, zinc blende, and rocksalt, as schematically shown in Fig.(1.8) at ambient conditions, the thermodynamically stable phase is wurtzite. The zinc-blende ZnO structure can be stabilized only by growth on cubic substrates, and the rocksalt NaCl structure may be obtained at relatively high pressures.

The wurtzite crystal structure and the projection along the [0001] direction are shown in Fig. (1.9) Even though it is tetrahedrally bonded, the bonds have a partial ionic character. The lattice parameters of ZnO are \( a = 0.32495 \) nm and \( c = 0.52069 \) nm at 300K, with a c/a ratio of 1.602, which is close to the 1.633 ratio of an ideal hexagonal close-packed structure. In the direction parallel to the c-axis, the Zn-O distance is 0.1992 nm, and it is 0.1973 nm in all other three directions of the tetrahedral arrangement of nearest neighbors.

![Figure (1.8)-Stick and ball representation of ZnO crystal (a) Cubic rocksalt (b) Cubic Zinc blende and (c) Hexagonal Wurtzite.](image-url)
This structure does not possess a center of symmetry. The lack of inversion symmetry in ZnO leads to piezoelectricity. The polarity of the c-axis results in the Zn-terminated and O-terminated planes displaying vastly different properties.

**Literature survey of ZnO thin films**

The assemblies of low-dimensional building blocks (nanodots, nanowires, nanobelts, and nanotubes, etc.) into hierarchical architectures on various substrates have attracted great interest because of the demands for many practical applications in functional devices. As one of the most important oxide semiconductor materials, ZnO has attracted considerable attention due to its good optical, electrical, and piezoelectrical properties and its potential applications in diverse areas. Various quasi-one-dimensional nanostructures of ZnO have been grown, including nanobelts, nanowires, nanotubes, etc. Meanwhile, various self-organized hierarchical ZnO nanostructures, such as nanorings, nanopropellers, nanobridges, nanonails, and nanocombs, have been synthesized by vapor-phase processes. The novel functions of these ZnO nanostructures arrays have been revealed successfully in the nanolasings, piezoelectric nanogenerators, nanoresonators, photonic crystals, photodetectcors, optical modulator...
waveguides, light-emitting diodes, field emitters, gas sensors, solar cells, and so on [70]. Films with well-aligned ZnO nanorods or nanowires may exhibit much larger surface areas than ZnO films prepared from randomly oriented nanoparticles. Moreover, these nanorods are packed very densely, enabling the fast and effective transport of electrons [71]. However, it still remains a big challenge to develop simple and reliable synthetic methods for hierarchical architectures with controlled morphology, orientation, and surface architectures, which strongly affect the properties of nanostructured materials.

Guo et al. [72] reported potentiostatic electrodeposition method for well-aligned ZnO nanorod arrays (ZNAs) under different conditions. It is indicated that the electrodeposition parameters, such as electrodeposition potential, electrolyte pH, concentration of precursors, temperature of solution and electrodeposition time, have significant influence on the morphology, diameter, density and growth rate of ZNAs. The growth temperature has great impact on the morphology of ZnO nanostructure but it is weakly related to the band gap (Eg) of ZNAs. Postels and co-workers [73] reported growth of zinc oxide nanorods in a zinc nitrate/hexamethylenetetramine solution at 70°C. In this configuration the nanorods are already contacted and electrical measurements can be directly performed. First I-V measurements show a good conductivity of the as-grown nanorods and the resistance could be estimated to be 0.1 Ω cm. Under UV illumination the ZnO nanorods demonstrate a photoconductivity, but only after annealing the sample at 300 °C in N₂. Chander et al. [74] reported the electrodeposition of ZnO nanorods from aqueous solution at low temperature (80 °C). Nanorods were grown by electrodeposition from aqueous solution of Zinc Nitrate and Hexamethylenetetramine (HMT). The nanorods have a well-defined hexagonal morphology and have a wurtzite structure.

Wang et al. [75] reported the preparation of three-dimensional (3D) mesoporous zinc oxide (ZnO) films and their application in solar cells. Results showed that the interpenetrating network of both ZnO(IO) and P3HT can form continuous pathways for electron and hole transport. By infiltrating a P3HT:ZnO nanocomposite into the porous ZnO films, the photocurrent of the
solar cell can be dramatically improved. The cell shows the $V_{oc}$ and $I_{sc}$ of 462 mV and 444.3 $\mu$A/cm$^2$ respectively.

Compact and transparent ZnO films were deposited on the ITO/glass substrates from zinc nitrate aqueous solution. The first step was used to produce ZnO seed layer, then ZnO film growth has been done. The film exhibits smooth and compact morphology, high transmittance in the visible band (>80%) and sharp absorption edge (at 370 nm) which was reported by Gao et al.[76] While Liu et.al [77] report a highly effective growth of vertically aligned ZnO one-dimensional (1D) nanostructures on conducting alloy substrate (Fe-Co-Ni) in mild solutions ($T \leq 70^\circ$ C) in the absence of any seeds, catalysts, and surfactants. Different ZnO single-crystal nanostructures including nanoneedles, hexagonal nanorods, and nanopencils oriented normal to the substrate can be selectively formed in high quantity. The ordered ZnO nanostructures show strong UV excitonic emissions and good field emission (FE) properties.

Lincot et al. [78] reported chemical deposition in solution and electrodeposition are emerging as a low cost, low temperature and large scale alternative to vapor phase deposition techniques for the elaboration of chalcogenide and oxides films. It is shown how solution chemistry concepts (complexation/precipitation, oxydo-reduction/precipitation) can provide a rational understanding of underlying growth mechanisms (CdS, CdTe, ZnO) and new routes for material synthesis.

Govender et al. [79] greatly reviewed the factors that govern the deposition and morphology of ZnO thin films from aqueous solution. The influence of the choice of complexing ligand, zinc counter-ion, pH, ionic strength, supersaturation, deposition time and substrate, on the nature of ZnO films grown from CBD has been greatly discussed. Yambai and Imai [80] reviewed the growth conditions for the wurtzite ZnO thin films in aqueous solution. Nanoscale ZnO grains and rods having various aspect ratios were selectively synthesized through acidic and basic routes, respectively, in an aqueous system at 323 K by Kawano and Imai [81]. Wang et al. [82] systematically investigated the solvent effect on the ZnO crystal growth and
film structure in the CBD process. They argued that, the aspect ratio of ZnO crystals formed was gradually decreased with increasing ethanol \([C_2H_5OH]\) content, leading to the transformation of rods into discs and in addition they have shown crystallite orientation in ZnO films was easily controlled. The nanorods in the films were found to become increasingly tilted as the \(C_2H_5OH\) content increased. Samanta et al. [83] have grown flowerlike bundles of ZnO nanosheets from aqueous solution of zinc nitrate \([Zn(NO)_3]_2\) and NaOH solution, with hexamethylenetetraamine (HMT) used as the ‘shape inducing reagent’, helps in preferential growth of ZnO nanostructures. Further, they have studied the violet light luminescence and optical absorption spectra throughout the visible part of the spectrum. Vertically aligned one dimensional (1-D) ZnO rods on Si coated wafers and vertically aligned two dimensional (2-D) ZnO sheets on aluminum flakes were fabricated in aqueous zinc chloride \([ZnCl_2]\) and HMT solution by Hua et al. [84]. Shinde et al. [85] have obtained the textured ZnO films onto amorphous glass substrate by CBD method from aqueous alkaline \([Zn(NO)_3]_2\) bath maintained at 353 K. Hubert et al. [86] studied the synthesis of zinc-oxy-hydroxide–sulphide \([Zn(S,O,OH)]\) films by CBD in a wide and well defined experimental parameter window. They have studied effect of the bath temperature and ammonia \([NH_4OH]\) concentration to study solution chemistry aspect. Further, they have studied solar cell properties using Zn(S,O,OH) as buffer layer. Wang and Xie [87] have synthesized nanostructured ZnO thin films via modified CBD by using small amount of citric acid as the organic capping molecules. Taking into account the low efficiency of CBD method, Lopez et al. [88] have tried to improve the efficiency of the CBD method using very small amount of \(ZnCl_2\) and other reagents such as \(NH_4OH\), \(NH_4Cl\), and \(H_2O_2\) etc. Yoon and Kim [89] have obtained nanostructured ZnO films were deposited onto different substrates such as (1 1 1)-oriented Pt, (2 0 0)-oriented Pt and amorphous silicon nitride on silicon wafers. They obtained strong dependence of the preferred orientation on the substrate and shown the substrate with small lattice mismatch shown the c-axis growth of the film. Sun et al. [90] have grown 2-D ZnO nanosheets onto Si substrate and pre-formed ZnO seed-layer at room temperature. Cao and Cai [91] have obtained ZnO nanostructures on Si substrate using \(Zn(NO_3)_2\) and dimetyamineborane (DMAB). They have shown
ZnO morphology evolves from nanorods to nanoplates, by changing the DMAB concentration.

Wang et al. [92] obtained the ZnO thin film with controlled orientation onto seeded glass substrate; they have studied the effect of volume ratio of H₂O to C₂H₅OH on the crystallite orientation of the films. Further, they have studied the low temperature photoluminescence for the thin films prepared in various H₂O/C₂H₅OH solutions. Hari et al. [93] have grown ZnO nanorods on indium doped tin oxide (ITO) coated glass substrates, by heating an equimolar solution of Zn(NO₃)₂ and HMT solution. The morphology of ZnO nanorods exhibited both open and closed hexagonal shapes by varying deposition time 4 – 26 hrs. Peiro et al. [94] have deposited ZnO nanorods on conducting glass substrate in relatively short deposition time. Structured ZnO thin films onto ITO coated glass substrates by chemical method obtained by Drici et al. [95], such films have been used in micro-structured solar cells with configuration ITO/ZnO/absorbant/aluminium. Mane et al. [96] have synthesized controlled growth of ZnO nanorods having thickness >10 µm, obtained by repeated chemical deposition. Hosono et al. [97] have synthesized ZnO rods with high density vertically aligned multistage terrace structure (HDVAMT) onto Au nanoparticle array covered ITO by CBD method. Further, they have shown the DSSC based on HDVAMT ZnO rods have the higher efficiency (10 times) than the disordered ZnO rods. The ZnO nanorods with high aspect ratio have obtained by Gao et al. [98], they could obtain ZnO nanorods with high aspect ratio by simply varying the amount of NH₄OH in the equimolar solution of ZnCl₂ and HMT grown onto the electrodeposited ZnO seeded layer. Further, the DSSC study of ZnO nanorods shows the conversion efficiency of 1.7 %. Kalkuchi et al. [99] have grown the ZnO nanosheets onto FTO coated glass substrate from aqueous solution of Zn(NO₃)₂ and urea [(NH₂)₂CO] and pH value can be adjusted by adding nitric acid. The ZnO nanosheets with thickness upto 3 µm were grown and have further used as the photoanode for DSSC application, shows the high conversion efficiency upto 3.3 %. Vayssiers [100] have fabricated well aligned, single crystalline ZnO hexagonal nanorods with diameter typically 100-200 nm wide and upto about 10 µm long were grown onto silicon wafer
and nanostructured ZnO thin films as the substrate. Further, by lowering the overall concentration of the precursor, the crystalline nanowires with diameter typically 10-20 nm wide and up to several µm long were identified after few hours of aging.

1.2.3 Survey of literature on CdS sensitized ZnO:

Sensitization is the process in which treatment of substance by heat, radiation or activating reagents to produce a more complex or rapid chemical and physical changes.

![Diagram](image)

**Figure (1.10):** Schematic diagram of the photogenerated charge transfer and loss pathways in Semiconductor/Quantum Dot Sensitized Solar Cells

The process involve following steps in SSSCs or QDSSc:

1. electrons inject into the conduction band of ZnO,
2. holes release to electrolyte,
3. electrons inject into electrolyte,
4. electrons and holes recombine in QDs,
5. and 6. electrons and holes are trapped by the surface states of QDs and recombine in traps,
7. electrons transfer back to electrolyte,
8. Trapped electrons escape to electrolyte,
9. electrons transfer back to QDs.
A semiconductor sensitization is like formation of the heterojunction between two semiconductors—one wide band gap and other narrow band gap. A semiconductor heterojunction is a junction between two chemically different semiconductors. Heterojunctions have been receiving attention for considerably long time because of their several useful applications as switching devices, solar cells, and in junction field effect transistors [101]. Literature survey of heterojunction during last 30 years revealed that, mostly heterojunctions were fabricated for photovoltaic applications. Initially heterojunctions were fabricated with inorganic semiconductors. These includes IV-IV group (Ge/Si) heterojunctions either n-p, p-p or n-n type on silicon substrate were studied from photovoltaic application point of view. Also IV-VI groups, II-IV group, II-VI group such as, Ge/Te, Si/Te of silicon or germanium crystal were fabricated. IV- (II-VI) semiconductors eg, CdS/ZnO, CdS/TiO$_2$, CdSe/ZnO, CdSe/TiO$_2$, Ge/ZnO, Ge/ZnS, Ge/ZnSe, Ge/CdS, Ge/CdSe, Ge/CdTe etc were fabricated. Heterojunctions fabricated using various methods among elemental or compound semiconductors at the beginning of heterojunction era are listed by Sharma et al. [102]. Among inorganic semiconductors heterojunction, CdS/CdTe is mostly studied. CdS/CdTe solar cells have been prepared by periodic pulse electrodeposition with 10.8% efficiency, open circuit voltage (Voc) = 753 mV, short-circuit current (Jsc) = 23.6 mA/cm$^2$ and fill factor (FF) = 0.61. Current-voltage-temperature measurements showed the variation of ideality factor from 1.88 at 344 K to 4.49 at 402 K [103]. The large lattice mismatch between CdS and CdTe is a potential problem, but there is evidence that thermal processing leads to formation of a mixed CdTe$_{1-x}$S$_x$ phase in the junction that overcomes this problem [104-108]. Investigation of non-aqueous electrodeposited CdS/ Cd$_{(1-x)}$Zn$_x$ to form solar cells with 8.3 % efficiency on ITO coated glass was reported by Chaure et al. [109]. Heterojunction based on inorganic-organic semiconductors are intensively studied due to their low cost and simplicity of technique used [110]. Organic semiconductors find place of inorganic one in their comparable electrical conductivity, good thermal and environmental stability, and ease of synthesis [111]. The use of conjugated polymer as device candidate is in practice during last two decades. First organic / inorganic thin film photovoltaic junction was made by Horowitz et al [112] who
studied a GaAs / polythiophene n- p junction. Then Franck et al. [113] investigated a CdS / P- me T (poly 3- methyl thiophene) Schottky junction. In both cases, solar to electrical conversion efficiency was limited by light absorption in polymer film.

Recently, vigorous demand for the electrical conversion efficiency focused on the PEC solar cells composed of varying band gap energies thin films that harness entire solar spectrum for the efficient photoperformance. A limited fraction of incident solar photons have sufficient energy to initiate charge excitation within a semiconductor. It is well accepted that the wide band gap semiconductors generate a high photo-voltage but have low photocurrent. Smaller band gap semiconductors can utilize a larger fraction of the incident photons but generate lower photovoltage. Therefore, it is believed that a device having multiple band gap energy layers can cover broad visible spectrum. In stacked multijunction systems, the top most semiconducting layer absorbs (and converts) photons of high energy, but is transparent to photons of lower energy and subsequent layer(s) absorb the lower energy photons [114,115]. Solar cells composed of multiple band gap semiconducting layers are capable of better matching and utilization of incident solar radiation. Multiple bandgaps, rather than single band gap semiconductor devices can provide more efficient matching of the solar spectra [116-118]. The semiconductor sensitized solar cells are the efficient way in which multiple band gap semiconductors provides light harvesting in visible region.

Zhang et al. [119] reported a versatile solution route for oxide/sulfide core shell nanostructures and nonlayered sulfide nanotubes. Large-scale, uniform and regular oxide/sulfide core–shell nanostructures and nonlayered sulfide nanotubes, such as ZnO/ZnS, SnO₂/SnS₂, MnO₂/MnS₂ core–shell nanostructures, as well as ZnS and SnS₂ nanotube have been prepared by a versatile approach based on a thioglycolic acid assisted hydrothermal process and subsequent NaOH treatment.

Leschkies et al.[120] have combined CdSe semiconductor nanocrystals (or quantum dots) and single ZnO NWs to demonstrate a new type of quantum dot sensitized solar cells (QDSSC) or semiconductor sensitized
solar cells (SSSC). They proved that the electrons are injected across the quantum dot–nano wire interface into the ZnO and the nanowires provide the photo-injected electrons with a direct electrical path way to the photo-anode. Furthermore, Tak et al. [121] have found that the CdS nanoparticle/ZnO nanowire heterostructure has enhanced photo-catalytic activity [122], because the CdS and ZnO can form a type-II heterojunction, which can efficiently separate photo-generated electron–hole pairs in each semiconductor material and reduce their recombination.

Lee and co-workres [123] reported that, CdS and ZnO can form a II-type semiconductor heterojunction, which can efficiently separate photo-generated electron–hole pairs in each material and reduce their recombination, and this was considered useful to enhance the PCE of (QDSSC). X. Song and co-workes [124] reported the effect of post-annealing on the conversion efficiency of solar cells sensitized by CdS quantum dots. The CdS quantum dots were deposited on ZnO nanowire arrays through a chemical bath deposition process. The thickness of CdS layer and the annealing temperature were found to be very crucial for the final performance of CdS/ZnO solar cells. The power conversion efficiency was improved significantly after annealing treatment, which can be attributed to the red-shift of the absorption edge of CdS quantum dots and the formation of a diffusion layer between the CdS shell and ZnO core. By the annealing treatment the light to electricity conversion efficiency was found to be 0.48%. The earlier report of same method but without annealing [125] shows the conversion efficiency of 0.34%.

Chen et al. [126] used CBD to synthesize bilayer ZnO nanostructure on ITO glass in the alkaline solution. As revealed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), the product consists of a layered structure of ZnO nanorods at the bottom and nanoflower atop. The as-prepared sample was assembled in QDSSC, which obtained the incident photon to current conversion efficiency (IPCE) of 15% at 400 nm and power conversion efficiency (PCE) of 0.45%. They concluded that, the novel bilayer ZnO nanostructure has the potential application in solar cell device as the photoelectode.
W. Lee et al. [127] formed CdS quantum dots (Q dots) on the vertically aligned ZnO nanorods electrode by CBD. The diameter and thickness of ZnO nanorods are about 100–150 nm and 1.6 µm, respectively, and CdS Q dots on ZnO nanorods have a diameter of smaller than 15 nm. In application of the Q dots sensitized solar cells, composite film exhibited a power conversion efficiency of 0.54% under air mass 1.5 conditions (80mW/cm²), and incident-photon-to-current conversion efficiency showed 18.6%. Lee and co-workers in his previous research work on use of Q dots in QSSCs [128-130], they describe a methodology for direct formation of CdS Q dots on ZnO nanorods by chemical bath deposition. Furthermore, CdS Q dots/ZnO nanorods films applied to Q dots-sensitized solar cells. Y. Tak et al. [131] reported the enhancement in PEC performance of SSSCs are due to their higher visible-light absorption capability and charge carrier transfer efficiency.

1.3 Purpose of the dissertation:

CdS is used as a buffer layer in the formation of solar cells devices based on CuInSe₂, CuInGaSe₂, CdTe. Recently, CdS nanoparticles are applied to Semiconductor Sensitized Solar Cells (SSSC) to improve the performance of wide band gap semiconductor materials. In SSSC, CdS nanoparticles form a layer on wide band gap semiconductors like ZnO, TiO₂ which, having nanostructured morphology, consisting of nanorodes, nanotubes, etc. CdS nanoparticles thin layer would be helpful for significant improvement in photoresponse in the visible region of CdS/ZnO or CdS/TiO₂ composite films. Also, the assemblies of low-dimensional building blocks (nanodots, nanowires, nanobelts, and nanotubes, etc.) into hierarchical architectures on various substrates have attracted great interest because of the demands for many practical applications in functional devices. As one of the most important oxide semiconductor materials, ZnO has attracted considerable attention due to its good optical, electrical, and piezoelectric properties and its potential applications in diverse areas. Films with well-aligned ZnO nanorods or nanowires may exhibit much larger surface areas than ZnO films prepared from randomly oriented nanoparticles. Moreover, these nanorods are packed very densely, enabling the fast and effective transport of electrons. However, it still remains a big challenge to develop
simple and reliable synthetic methods for hierarchical architectures with controlled morphology, orientation, and surface architectures, which strongly affect the properties of nanostructured materials.

The use of a semiconductor instead of a dye to sensitize the nanoporous oxide film received to impart some advantages to the cells, mainly higher absorption of the semiconductor coating compared with a single molecular layer of dye, greater stability of the semiconductor compared to organo-metallic or even pure organic dyes, and tailoring of optical absorption over a wider wavelength range than possible with dyes due both to the inherently wider band-gap range of semiconductors as well as the ability to tailor the band-gap by size quantization. However, in spite of these potential advantages, the solar efficiency of liquid junction SSSCs has reached only 2.8% at present.

A surfeit of physical and chemical methods have been used for the synthesis of CdS, ZnO or CdS sensitized ZnO nanostructures including high temperature chemical and physical vapor depositions, RF magnetron sputtering, spray pyrolysis, chemical bath deposition, hydrothermal process, metalorganic vapor-phase epitaxial growth, sol gel, etc. Chemical bath deposition is of particular interest due to low cost, environmental friendly, and feasibility of room temperature growth. It has been shown that CdS and ZnO thin films can be deposited by CBD and have high structural quality. We have demonstrated a soft chemical route that enabled the formation of the compact, large effective (photoactive) surface area and defect-free CdS, ZnO and CdS sensitized ZnO photoelectrodes, suitable for PEC solar cells.

The central idea of this work is to test the applicability of simple and inexpensive CBD technique as an update on previously studied methods for the synthesis of CdS, ZnO and CdS/ZnO thin films. In the present investigation the main aim is to synthesize CdS/ZnO nanocrystalline thin films and to enhance photoelectrochemical performance. In this direction attempts were made to deposit CdS/ZnO nanocrystalline thin films by varying various process parameters by using CBD. An attempt has also been made to obtain
a novel morphology of CdS, which enable effective light trapping, absorption and harvesting.

1.4 Plan of the work:

We learnt from the literature survey and theoretical background that the scientific problem of nanostructured CdS/ZnO thin films is of great importance for the future nanosize devices and for PEC applications in solar cells. Accordingly the work has been planed with following objectives-

1) To deposit good quality CdS nanostructured thin films using CBD by optimizing parameters such as precursor concentration, deposition temperature, pH, etc. Special emphasis is to be placed on novel morphology for the effective light harvesting.

2) To deposit good quality ZnO nanorods thin films using aqueous chemical method (reflux method) by optimizing parameters such as precursor concentration, deposition temperature, pH, etc.

3) To deposit high quality CdS nanoparticles sensitized ZnO nanorods thin films using CBD and study of their detailed structural, electrical and optical characterization. Testing of PV performance of CdS sensitized ZnO thin films.
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