Introduction

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1.1 The Energy Crisis

"The world has enough for everyone's need, but not for every man's greed" these are Mahatma Gandhi's words worth recalling at this time when we witness paradigm shifts in energy policies of many countries. Man is profligate with his energy resources, often detrimental to his surroundings. He has devised myriad ways to expend energy, but has only a handful of methods to generate energy. Over the years, the evolutionary processes in the name of technological growth have utilized energy to convert it into work useful for the life and hence the energy as an instrument for sustainable development is always needed. To cope with the increasing population on this planet, the demands result in development of need-based uses and services that are based on energy efficient as well as eco-friendly technologies. Considering the abuse, the man is making to the environment there is a need of developing 'green' alternative energy resources, which can ensure the secure and decentralized energy supply as well as protect us from evil effects.

The energy has acquired significant importance in the recent years due to the 'world energy crisis' which have been generated due to depletion of conventional fossil fuels. The 'world energy crisis' is observed because of increased demands of energy. In ancient times the energy resources were many and end users were limited, due to this the energy consumption was low. But today this picture has completely changed, as the need of energy is increased in such a great proportion that it is impossible to get instant solution to this problem. In many developed countries increasing demands of energy are met by import. These demands may fulfilled by number of alternative energy sources such as hydroelectric, thermal, wind and nuclear. But among these sources some are costly, time consuming and depleting with fast rate, while some are intermittent and depend on the whim of nature. These energy needs vary with life-style, climatic conditions, and seasons and with industrial progress wars. Thus today, every country draws its energy needs from a variety of sources through commercial as well as non-commercial methods. In industrialized countries most of the energy requirements are met mainly from

commercial sources, while in developing countries use of commercial and non-commercial sources are almost equal [1-2]. As the non-renewable energy sources create pollution and environmental consequences, it is a need of the day to use and develop the conventional technologies, by proper modification. As the environmental restrictions are being made more stringent all over the world, resulting in the new energy technologies now a days. Thus new pollution free and risk free energy technologies like solar energy, wind energy conversions are are being developed and implemented.

During the past several decades, the energy demands of the world have continued to increase at an annual rate of 3 to 4%. This is due to following reasons:

i) Sharp increase in population,

ii) Increase in rate of transportation,

iii) Increase in per capita energy consumption due to increasing standard of living

iv) Development of energy supply systems and

v) Increasing industrialization.

Thus solar energy is hope to fulfill the world's future energy needs with minimum adverse environmental consequences. Scientific basis for the utilization of solar energy was acquired some years ago, but till today it is not considered technologically feasible to make use of it on large scale. The problem is how to harness the energy obtained from the Sun efficiently and effectively.

The recent years have witnessed the use of technological and scientific progresses in the field. Some success has been achieved in large-scale utilization of solar energy. It has been observed that there is an enormous shift in the economics of power production, due to use of conventional processes for energy generation. Community needs are best illustrated by the demand electric power, now it is difficult to live without the supply of sufficient amount of electricity. The development of solar energy conversion in offering the best prospect for an unlimited supply of energy.

1.2 The Present Conventional and Non-conventional sources of energy:

There are three types of energy sources i.e.

1) Primary energy source,
2) Secondary energy source and
3) Alternative energy source.

The primary energy source includes conventional and non-conventional energy resources [3].

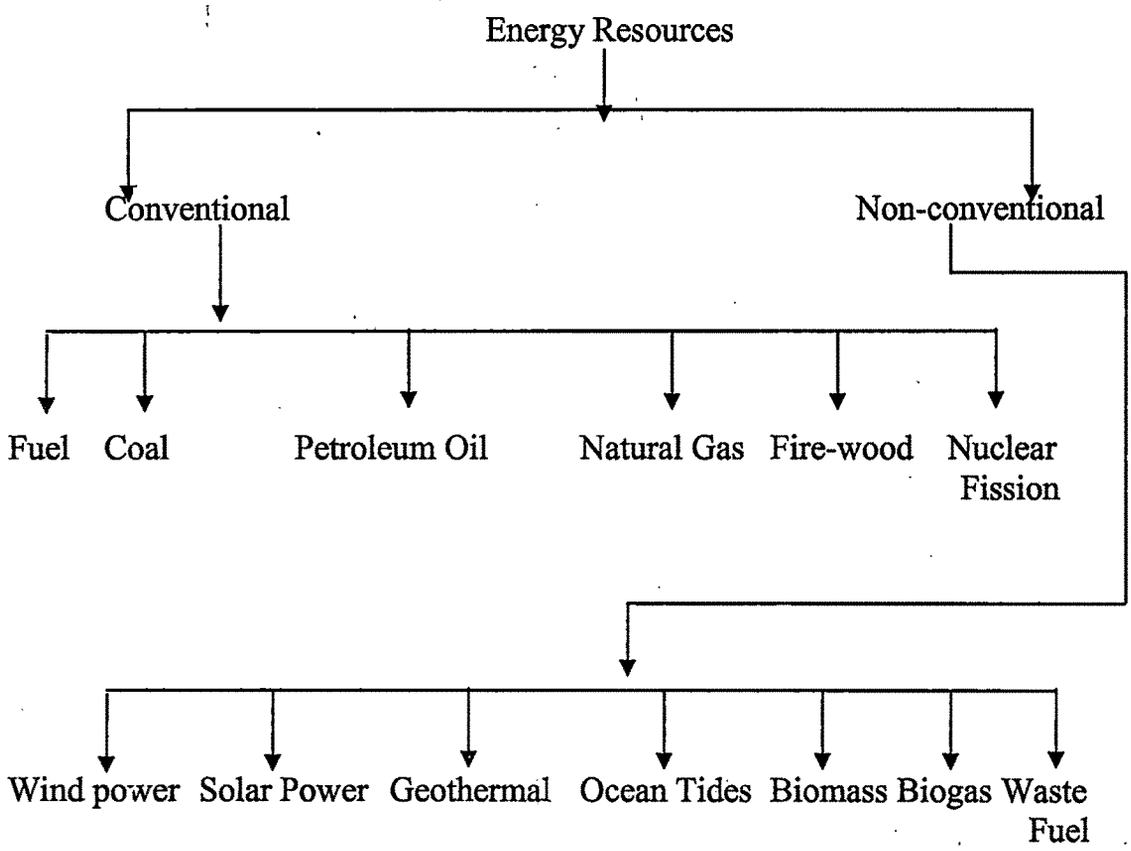

Fig: 1 Chart outlines the various energy resources.

Renewable or non-conventional energy resources are those, which are renewed by the nature again and again, and the supply is not affected by rate of consumption. Renewables are renewed in the nature periodically.

Non-renewable or conventional energy resources are those, which do not get replenished after their consumption. For example coal, once burnt is consumed without replacement of the same. The conventional energy resources are formed very slowly in nature and are not regenerated and their reserves go on depleted due to consumption.

1.3 The Sun and Solar Energy:

It's a fact that all the biological processes are depending on the Sun. The production of food and regeneration of oxygen would be impossible without solar energy. Farmers know the value of large fields with an abundant supply of sunlight, and now individuals all around the world are taking this boundless source of diffuse energy more seriously as the finite supply of fossil fuels dwindle.

The energy from the Sun varies from place to place and is very dependent on weather conditions. The Sun is, at present has about 70% hydrogen and 28% helium by mass, everything else amounts to less than 2%. This changes slowly over the time as the Sun converts hydrogen to helium in its core [4]. Each second about 7 X 10^8 tonne of hydrogen is converted into about 6.95 X 10^8 tonne of helium and 5 X 10^6 tonne of energy is ganerated in the form of gamma rays. As it moves toward the surface, the energy is continuously absorbed and re-emitted at lower and lower temperatures so that by the time it reaches the surface, it is merely transformed into visible light.. The Sun is about 4.5 billion years old and since its birth it has used up about half of the hydrogen in its core,it will continue to radiate "peacefully" for another 5 billion years or so.

The Sun is a gigantic, continuous, pollution free and permanent source of energy .The Sun's outer visible layer is called the photosphere and has a temperature of 6 X 10^3°C (1.1 X 10^4°F). Solar energy is created deep in the core of the Sun with a temperature 1.5 X 10^6°C; 2.7 X 10^6°F. The Sun produces 4x 10^{26} W as electromagnetic radiation and a fraction of this is received by the Earth. The source of this energy is a series of reactions that convert four protons into one helium nucleus and 26.7 MeV of energy appears in the reaction.

The energy flow through the Sun is maintained by the basic nuclear reaction chain as shown in the fusion sequence [5].

$$ {}_1H^1 + {}_1H^1 \longrightarrow \underset{\text{Duteron}}{{}_1H^2} + \underset{\text{Positron}}{{}_1e^0} + \text{Energy} $$

$$_1H^2 + {}_1H^1 \longrightarrow {}_2He^3 + \text{Energy}$$

Isotope of Helium

$$_2He^3 + {}_2He^3 \longrightarrow {}_2He^4 + 2\,{}_1H^1 + \text{Energy}$$

Helium

Thus overall nuclear reaction may be written as,

$$4\,{}_1H^1 \longrightarrow {}_2He^4 + {}_{+1}e^0$$

Positron

These fusion reactions occur only at the core of the Sun where the high temperature (~10^7 K) gives the hydrogen and helium isotopes, enough kinetic energy is generated to overcome the long-range repulsive Columbic forces and come within the short-range of the attractive strong nuclear force. The reaction energy slowly percolates to the surface of the Sun and then it is radiated mainly in the various regions of the electromagnetic spectrum. Only the neutrinos escape from the Sun without giving up their energy.

The reaction needs no supply of fuel and produces no waste or pollutants. The solar energy reaching down to earth's surface in a forenight, amounts to 10^{16}KJ/m^2. The electricity falling on an area of 8 km^2 is approximately equal to the output of whole India's electricity generating system. This superfluity of energy makes solar energy research extraordinarily challenging. Solar energy alternatives are less expensive than fossil fuels and grid power. The indications are that the solar energy is one of the most promising conventional energy resources. Today less than 0.1% of our heating, transportation and electric energy comes from the direct sunlight although it seems possible to meet all our energy needs with this simple, renewable resource.

1.4 Recent technologies in solar energy conversion

Thin film technology has its objectives in the provision of scientific bases for the methods and material used in thin film electronics. It plays vital role in the development of diverse and challenging frontiers such as microelectronics, thin film superconductivity, optical coatings, surface engineering and amorphous materials [6-9]. Now more exciting fields are

emerging from the origin of such frontiers, and lies in the exciting phenomenon of micro science associated with low dimensional micro and nano materials and industrial applications such as the VLSI or GSI communication, informatics and a solar energy conversion [10-15].

1.4.1 What is Thin Film?

The materials we see around us are bulk materials with all their dimensions in the macroscopic scale. A thin film has its dimensions in the macroscopic scale only along its length and breadth. Thin film can be defined as any solid or liquid system possessing at the most two-dimensional order or periodicity .The properties of thin film often significantly differ from those of bulk due to surface and interface effects, which may dominate it is overall behavior. The thin film can be single or multicomponent alloy, compound or multilayer coatings. Due to their potential technical value and scientific curiosity in the properties of a two-dimensional solid, thin films have been extensively studied for over a century.

The prominent physical phenomenons of the thin films are generally the consequences of their planar geometry, size and structure. The microscopic viewpoint of thin film phenomenon to solid-state physics has injected a new intellectual vigor into electrochemistry and surface chemistry. A lot of interest has been developed in the synthesis of thin films, which are capable of collecting and storing the solar energy. In principle this is an extremely important area of research, because the total amount of solar energy that falls on the earth's surface per year overweighs our present or near future energy demands. However there are many barriers to overcome before such devices transform into reality. In fact till date, we have not yet identified all the problems involved in the construction of practical solar energy converting and storing devices. For this purpose a number of techniques have been developed. All the methods have their own advantages and disadvantages.

1.4.2 Various Deposition Techniques:

The properties of thin film essentially depend on the method of preparation. A large number of techniques have been developed for deposition of the thin films [16].

The basic steps involved in thin film formation are -

a) Production of material to be deposited in atomic, molecular or ionic form.

b) Transport of materials thus created.

c) Deposition of film by nucleation and growth process.

Each technique has its own advantages and disadvantages. Therefore every time new method is developed by overcoming disadvantages of previous methods .The techniques have been differentiated into two types:

1. Physical vapour deposition (PVD)
2. Chemical deposition techniques (CDT)

1. Physical vapour deposition:

This is the technique in which the material to be deposited is made available in the atomic, molecular or particular form before deposition. The condensation of such material on substrate material kept at relatively low temperature yields a thin film. PVD can be classified as:

a) Thermal evaporation,

b) Electron beam evaporation,

c) Molecular beam evaporation,

d) Activated reactive evaporation,

e) Ion plating,

f) Sputtering.

The detailed description the physical methods are beyond the scope of this thesis.

2. Chemical Deposition Techniques:

The thin films prepared by using chemical deposition techniques have great importance because of its feasibility depositing a large number of elements and compounds at a low temperature as compared to other methods.

The Chemical deposition are techniques are classified as follows:

1) Electrodeposition,
2) Anodization,
3) Spray pyrolysis,
4) Chemical vapour deposition,
5) Chemical bath deposition,
6) Screen printing.

1) Electrodeposition

In this technique, the deposition of material is carried out on electrode by electrolysis process. The chemical change is brought about by passing electric current through electrolyte. During deposition, ions reach at the respective electrode, stabilize on it; release their charges and undergo electrochemical deposition.

2) Anodization

In this the metal is made of anode in suitable electrolyte. The pH of electrolyte plays a vital role in the deposition.

3) Spray pyrolysis

This technique consist of thermally stimulated reaction between clusters of the liquid or vapour atoms of different spraying solutions of desired compounds onto a substrate maintained at higher temperature. The fine droplets reaching at the hot substrate undergo pyrolytic decomposition and deposited on it.

4) Chemical Vapour deposition

In this technique, a solid or liquid compound is made gaseous by volatilization and allowed to flow either by a pressure difference or by carrier gas to the substrate.

5) Chemical bath deposition

The method includes growing of film on any suitable substrate by dipping it in appropriate solution of metal salt. The cation of respective metal, complexed with suitable complexing agent is allowed to react with chalcogen ion. The cations and anions so produced combine on substrate via nucleation.

6) Screen printing

By using this technique thick film deposition can be carried out. For this the desired material is screen printed by conventional method onto a suitable substrate.

The chemical bath deposition technique is mostly used for deposition of various elements. It is also known by various names as 'electroless plating' or 'precipitation method'. The technique of chemical bath deposition involves the controlled precipitation from solution of compound on a suitable substrate. In this method the substrate is immersed in the precursor solution. The deposition occurs either by homogenous or heterogeneous chemical reaction. The film formation takes place when ionic product exceeds the solubility product.

This technique has many advantages over other techniques to fabricate semiconductors such as chemical vapour deposition, molecular beam epitaxy and spray pyrolysis.

1) Chemical bath deposition is an inexpensive, simple and convenient method for large area deposition of thin films.
2) The technique works at low temperature i.e. less than 90^0C.
3) There is no limitation on choice of substrate material as it operates at low temperature.
4) In chemical bath deposition technique, film thickness and deposition rate can be controlled by varying the pH of solution, reagent concentration, and temperature.
5) The oxidation or corrosion of the metallic substrate is avoided by using low temperature.
6) As the process of thin film growth is slow, it facilitates better orientation of the crystallites with improved grain structure.
7) Pin hole free and uniform deposits of complex shapes and sizes can be obtained due to intimate contact between the reacting solution and the substrate material used.
8) The basic building blocks are ions instead of atoms which maintain the stoichiometry of deposits.

9) The method does not use any toxic volatile constituents.

10) By using chemical bath deposition the doped and mixed film structure can be obtained very easily by adding dopant solution directly into reaction bath.

11) In this method, electrical conductivity of substrate material has no great importance.

12) This method can be used for deposition of elementary, binary, ternary or quaternary thin films.

13) The technique is applicable for the deposition of highly insoluble compounds.

1.5 Solar Cells

The solar cell has been one of the critically important devices in the space program. Energy conversion devices, which are used to convert sunlight to electricity by the use of photovoltaic effect. In the recent years photovoltaic power generation has been receiving considerable attention as one of the more promising energy alternative because it shows non-polluting nature, non-dependence on fossil and nuclear fuels.

Solar cells were developed during 1950s, primarily at the Bell Telephone and RCA Laboratories [17]. Photovoltaic effect can be observed in almost any junction of materials that have different electrical characteristics. But the best performance to date has been from cells using semiconductor materials. When the Sun's rays i.e. Sun's photon flux, strikes a p-n semiconductor junction, they help to generate electron-hole pairs. Thus it causes the electron to be raised to conduction band and holes to be moved to the valence band, when connected to the load.

1.5.1 Theoretical Considerations:

Fig. 1.1 shows schematic of a typical solar cell showing the physical arrangement of major components [18]. If electrical contacts are made with the two semiconductor materials and the contacts are connected through an external electrical conductor, the free electron will flow from the n-type material through the conductor to p-type material. In this the free electrons will

enter the holes and become bound electrons. Thus both free electrons and holes will be removed. The flow of electron will be continue as long as more free electrons and holes being formed by the solar radiation. This is the basis of photo-voltaic conversion that is, the conversion of solar energy into electrical energy.

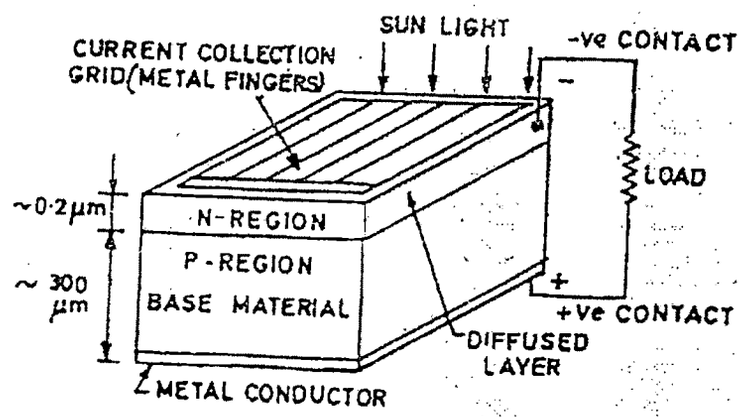

Fig. 1.1 Schematic of a typical solar cell showing the physical arrangement of major components

The combination of n-type and p-type semiconductors thus constitutes a photovoltaic cell. All such cells generate direct current, which can be converted into alternating current.

1.5.2 Historical Development of solar cells:

The discovery of solar cell has taken a span of about hundreds of years after the discovery of selenium by Berzelius in 1817. Becquerel [19] first observed this in 1839 that, 'the Photovoltage was developed when light was directed on to one of the electrodes in an electrolyte solution'. It was followed by the discovery of photoconductivity in selenium by Willoughby Smith in 1873. Adams and Day [20] were the first to observe the photovoltaic effect in solid state selenium, in 1876. Lange [21], Grondahl [22] and Schottky [23] did the pioneering work on the selenium and cuprous oxide photovoltaic cell. Hallwaches in 1904 first observed the photosensitivity in copper-cuprous oxide system. In 1914, the photovoltaic effect was first time connected with the existence of a barrier layer. Fritts described the first photovoltaic cell. With the progressing development of the silicon technology, the grown p-n junction

technique led to the preparation of single crystal silicon photovoltaic device in 1941. The first solar cell was developed by Chapin in 1954 using diffused silicon p-n junction [24]. In 1954, Reynolds, Leies, Antes and Marburger [25] reported solar cell of efficiency of about 6%in cadmium sulphide p-n junctions.

In 1955 Reynolds et al developed cadmium sulphide solar cells. Pfann and V. Rosbroeck Prince developed solar cell theory. Later on in 1958 Sah, Noyce and Schokley developed improved p-n junction theory. Then Loferski, Rapaport and Linder [26] developed theory for solar cell efficiency and band gap. Wolf gave spectral response theory and loss mechanism. Wysocki acquired success in development of self-annealing lithium containing silicon cell in 1966. In 1967, Shiozawa *et al* gave model of Cu_2S-CdS solar cell. The silicon single crystal photovoltaic cell had been used for many years due to its efficiency. This silicon single crystal material is focussed attention and used in solar energy conversion system. This technology of silicon single crystal solar cell was not attended properly for long period of time because of its high cost of production. If we expended this high cost, we could not get expected efficiency from it. Therefore this work was not commercialized. Although use of various technologies reduced the cost of production, most of workers devoted their research for the development of solar cells by using material other than silicon.

The new technology of photovoltaic cell was developed containing semiconductor electrode, counter electrode and electrolyte. The credit of first development of PEC cell goes to Gerischer [27] in 1960. Hovel had given a comprehensive treatment on basic solar cell characteristics [28]. Fujishima and Honda [29] achieved solar cell efficiency of 4.8% in 1972. For this CdS/Cu_2S heterojunction was used. Backus has complied a volume of classical papers on solar cells in 1976 [30]. Binary semiconducting materials like CdSe, PbSe, ZnSe, CdTe, $MoSe_2$, SnS and ternary semiconducting compounds like $Cd_{1-x}S_xSe$, $Pb_xCd_{1-x}Se$, $Hg_xCd_{1-x}Se$ etc have been studied [31-36].

1.5.3 Kinds of Solar Cells:

Solar cells can be classified into various types depending on the nature of junction formed,

1. The Semiconductor – Semiconductor junction cells

These are classified into,

a) Homojunction

b) Heterojunction

If the two semiconductor materials are derived from the same element the system is known as a homojunction. In case of heterojunction the p-n junction is formed from two different semiconductor materials.

2. The semiconductor –metal (S-M) junction cells / Schottkey junction

The Schottkey junction consists of a semiconductor and metal. Deposition of a thin layer of metallic conductor onto a p or n-type semiconductor forms the junction. Schottkey junction photovoltaic cells made with the so-called amorphous silicon are more efficient than the homojunction p-n cells.

3. The M-I-S and S-I-S solar cells

These cells consist of thin interfacial layer (10-30A^0) between a top inducing contact (metal or semiconductor) and the base material (semiconductor). An interfacial layer is generally an oxide or some other compound is always an insulator.

i) Photoelectrochemical cell

In the PEC cell, the photoinduced electron hole pairs are used to generate electricity in the solid state solar cells. The photoassisted reaction that takes place at the semiconductor electrode is reversed at the counter electrode.

ii) Photoelectrolytic cell

In the photoelectrolytic cells, the light energy is converted into chemical energy. The photogenerated hole is used to oxidize the electrolyte species, while the electron to reduce other. The reaction is chosen such a way that the product can be stored and when they are subsequently reacted and the energy can be recovered. An important application of this cell is the

photodecomposition of water to generate the fuel hydrogen [37-40]. The photogenerated hole oxidizes the OH^- ion to O_2 gas while electron reduces H^+ to H_2 gas. In this case the external circuit is short circuited to ensure free flow of current.

iii) The rechargeable cells

Now more efforts are being taken to produce the rechargeable photoelectrochemical cells. Such a cell resembles the storage batteries except that the charging is carried out by light rather than power supply. In this system two redox electrolytes are used and separated by either an ion selective membrane or a salt bridge. On illumination, one of the redox systems is oxidized at the n-type semiconductor electrode while another redox system is reduced at counter or p-type semiconductor electrode. In dark, the reverse reaction takes place [41-50].

iv) Photogalvanic cell

In these cells the electrical power is generated by charge transfer from excited species to electrodes in contact with light absorbing system. These are the concentration cells where the effect of the light energy is felt within the solution. In these cells, photo energy is converted into an electrical energy by means of absorption of the photons by molecular species in the solution. The Photogalvanic effect is due to change in the current potential characteristics of electrolyte or electrode half cell produced by photolysis of the solution. Such effect is expected in any photochemical reaction which alters the concentration of any component of the solution to which the photoelectrode is responsive.

v) Photoelectrocatalytic Cell

In these cells the semiconductor is irradiated and the generated electrons and holes move to the surface, the hole oxidize the species at the surface while electrons reduce. Due to this chemical changes occur in the medium. Such a photoinduced chemical change is called as photoelectrocatalytic effect. These systems have few advantages as compared to other cells [51].

1.6 Literature Search

1.6.1 Literature Search of CdS thin films

Cadmium sulphide is an important material for the development of various modern technological solid state devices such as solar cells and high efficiency thin film transistors. Major attention have been given in recent years in the investigation of electrical and optical properties of CdS thin films in order to improve performance of the devices and also finding new applications. Various chemical preparative techniques such as, spray pyrolysis, eletrodeposition, SILAR, chemical bath depositions etc. are available for cadmium sulphide thin films. Among these methods chemical bath deposition is most important.

Cardona et al [52] have studied the reflectivity measurements at room temperature and observed that the two phases have band gap energy differing of less than 0.1 eV. Khawaja and Tomlin [53] have studied the behaviour of CdS thin film over the wavelength range 250nm to 2000 nm by measurement for reflectance and transmittance at normal incidence. Aray et al [54] have reported the deposition of low resistivity cadmium sulphide films using single source evaporation technique. Dawar at al [55] showed the low resistivity and high mobility of CdS films grown on glass, mica and silica substrate by vacuum evaporation.

The photoelectric and thermal properties of vacuum deposited CdS thin films were studied by Mohammed and Nory [56]. Nair *et al* [57] reported the conversion of photosensitive CdS thin films to more p-type by air annealing and ion enhance reaction, which are prepared by chemical bath deposition. They also studied the dark and photoconductivity measurements of the annealed films. The cadmium sulphide thin film is a promising semiconductor material, it can be used as solar window material for application in solar cells. Thin films of CdS prepared by controlled precipitation technique have been studied for their structural, optical absorption, electrical properties using XRD, , SEM, while several workers have also reported EDAX.

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Nel et al [58] have reported the microstructure of electrodeposited CdS layer from aqueous solution onto two different substrates. The investigations on electronics quality of chemical bath deposited layer were the main objectives of work by Dharmadasa et al [59]. For measuring electrical properties of Gold / CdS Schottky contacts were used. Dona and Hererro [60] have reported chemically deposited CdS layers from cadmium sulphate and thiourea and studied their electrochemical open circuit voltage, behaviour.

Hashimota [61] deposited CdS from Iodide containing chemical bath. It has been revealed that the film contains 3% iodine, while those grown in presence of cadmium chloride contains less that 1% iodine. XPS study showed a uniform distribution of these impurities in films. The presence of iodine as impurity in CdS film has been shown to improve CdS / CIS /Substrate cell performance. Cadmium sulphide thin films were prepared at high temperature by different scientists [62-66]. The room temperature deposition of CdS was carried out by Roy et al [67].CdS thin films were deposited onto glass, Ti ,FTO coated glass substrate by using cadmiumsulphate, thiourea and ammonium hydroxide. Crystallite size was controlled by reaction time, pH and temperature. Band gap was found to be 2.4eV for bulk and 2.97eV for nanocrystalline sample [68-70].

V.V. Ison et al [71] had grown the cadmium sulfide and cadmium telluride thin films by spray pyrolysis. Chemically pure, stoichiometric cadmium sulphide (CdS) films were produced by the chemical bath deposition (CBD) method on suitably cleaned silicon (Si) wafer and indium–tin oxide (ITO) substrates at room temperature [72]. The nanocrystalline film was found to be hexagonal in structure with the preferential orientation along the (0 0 2) plane. E. Çetinörgü et al [73] were deposited CdS films of over 1μm thickness onto glass substrates by chemical bath deposition. Annealing in air resulted in a shift of the absorption edge towards higher wavelengths, i.e., a decrease in the gap value from 2.45 eV to 2.38 eV. The optical band edges of the films were not constant but depended on the annealing temperature. The deposition

temperature and time were varied from 40 °C to 60 °C and from 30 min to 4 h, respectively.

A comparative study of deposition methods was studied by J. Hiie et al [74] by depositing CdS films on glass and ITO-covered glass substrates by two techniques as chemical bath deposition and spray pyrolysis technique. For this purpose $CdCl_2$ and thiocarbamide were used as basic precursors in both cases. As a result of annealing optical band gap (E_g) for chemical deposited CdS shifted from 2.51 eV down to 2.42 eV, whereas the E_g of sprayed films (2.46 eV) did not change. All the films have high transparency over 80% in the visible spectrum (520–850 nm). J.N. Ximello-Quiebras et al [75] had reported a study of the growth rate and optical properties of CdS thin films prepared by the chemical bath deposition technique. The growth kinetics is relatively fast when the quantity of thiourea is increased in the deposition solution and higher value of band gap is obtained (Eg= 2.44 eV). The films show good transmittance in the visible region.

S. Prabahar and M. Dhanam had grown the cadmium sulphide (CdS) thin films of different thicknesses by the chemical bath deposition technique (CBD) onto well-cleaned glass substrates at 80 °C from two chemical baths of different pH values 10 and 11 [76]. Physical properties of chemical bath deposited CdS thin films were studied by J. N. Ximello-Quiebras et al [77]. The XRD patterns show that the films have a hexagonal phase with a preferential (0 0 2) orientation. The photoluminescence spectra show a defect structure, characteristics of the CdS films obtained by chemical bath deposition. The effect of annealing on chemically deposited CdS thin films were studied by H. Metin and R. Esen [78]. The energy gap of the films was found to decrease by annealing. The best annealing temperature for chemical deposited grown CdS films was found to be 300°C from the optical properties. Optical properties of the films were calculated using the envelope method. Annealing over 300°C was seen to degrade the optical properties of the film. Electrical and optical properties of boron doped CdS thin films prepared by chemical bath deposition were studied by Jae-Hyeong Lee et al [79].

Polycrystalline CdS films, with thickness typically 20–180 nm, have been chemically deposited on glass substrates using an ammonia–cadmium–thiourea reaction solution [80]. The elemental composition, thickness and microstructure of film have been examined using proton-induced X-ray emission, Rutherford backscattering and atomic force microscopy. G. Sasikala, P. Thilakan and C. Subramanian [81] had reported growth and characterization of CdS thin films by chemical bath deposition (CBD) technique using the reaction between $CdCl_2$, $(NH_2)_2CS$ and NH_3 in an aqueous solution. XRD studies on the CBD–CdS films reveal that the change in Cadmium ion concentration in the bath results in the change in crystallization from cubic phase with (1 1 1) predominant orientation to a hexagonal phase with (0 0 2) predominant orientation. The structural changes due to varying cadmium ion concentration in the bath affect the optical and electrical properties. Optimum electrical resistivity, band gap and refractive index value are observed for the annealed films deposited from 0.8 M cadmium ion concentration.

1.6.2 Literature Search of PbS thin films

As the chemical bath deposition technique has comparatively low disadvantages, it can be used for the deposition of thin film material. The chalcogenides films of II-IV and IV-VI have already emerged as the potential materials of high performance and low production cost. Chemical bath deposition is a technique in which thin semiconductor films are deposited on substrate immersed in dilute solutions containing metal ions and a source of hydroxide, sulphate ions. The earliest reported work dates back to 1919 and dealt with the deposition of PbS thin films [82]. M. Madhusudan et al deposited mixed NiS-PbS and NiS-CdS thin films on commercial aluminum and galvanized iron substrates by spray pyrolysis [83]. Banyai et al [84] predicated that for a given particle size, the non-linearity of PbS would be 30 times larger than that of GaAs. The first chemically deposited semiconductor thin films of PbS and PbSe obtained by Bodes et al [85]. P.K. Nair et al reported the photoccelerated chemical deposition on PbS thin films, in which the illuminated region in a growing thin film showed accelerated deposition [86].

The first polycrystalline PbS films were obtained by vacuum evaporation. In 1948, F. Kicinski [87] reported chemical bath deposition technique for obtaining good quality films, giving large area deposition. Several changes such as changing the bath composition by adding oxidants and reductant or small amounts of metal ions can lead to important variations of photoconductive properties [88-92]. Reddy et al [93] deposited PbS films by solution growth technique using solutions of lead acetate, thiourea on Ni, Cu, stainless steel and glass substrates.

Nair et al [94] have reported the chemical deposition of PbS using lead acetate, thiourea, and ethanol amine (complexing agent). Sharma et al [95] have prepared copper doped PbS films and studied the dependence of structure, electrical conductivity and carrier mobility with doping. Irris et al [96] reported the influence of H_2O_2 on the crystalline orientation of chemically deposited PbS thin films. Nair et al [97] have studied solar control applications of chemically deposited PbS thin films. Nascu [98] et al studied influence of oxidant on the chemically deposited PbS thin films. Pop et al [99] have chemically deposited substrate from alkaline bath containing lead nitrate, thiourea and different additions such as hydroxylamine hydrochloride, triethanolamine and hydrogen peroxide. The sensitivity of chemically deposited PbS thin films have been studied by Pintillie et al [100] on poled and up poled ferroelectrics substrate. Fainer et al [101] have grown the PbS and CdS thin films by using low-pressure chemical vapour deposition-using dithiocarbamates. From this study they have shown that the activation energy of CVD process of thin film growth is 191.5 KJ mol^{-1}.

Najdoski et al [102] used elctroless chemical deposition for preparation of thin solid films of lead sulphide. The films were deposited on a glass substrate previously coated with thin layer of Cu_2S. They studied the optical & and electrical properties of PbS films. P.K. Nair [103] prepared thin films of PbS-CuS from solution containing Pb^{+2} and Cu^{+2} by chemical bath deposition. The important feature of these films is their good adhesion to glass substrate

even at long durations of depositions. For the deposition purpose lead acetate, copper chloride, sodium hydroxide and triethanolamine were used.

S. Abe et al [104] studied the growth and characterization of Bi-doped lead sulphide thin films prepared by hot wall epitaxy. The high carrier concentration is obtained above 10^{19} cm^{-3} with the n-type conductivity due to the doping of Bi in the films. In this study the diffraction pattern exhibited that PbS, Bi_2S_3 solid solution semiconductor has NaCl structure. The XPS studies of PbS nanocrystal doped SiO_2 thin films was reported by R. Reiche et al [105]. They studied the photoemission properties of PbS -SiO_2 composite samples.

The effect of indium doping on lead sulphide films was studied by R.S. Parra et al [106] .For the deposition of PbS thin films, corning glass substrates (75 x 25 mm and 1mm thick) were used. The chemical bath was prepared by mixing 1M lead acetate, 1M sodium hydroxide, and 1M-thiourea solution. The X-ray diffractogram of films annealed at various temperatures were recorded.

R.A. Orozco-Teran et al [107] used chemical bath deposition technique for PbS-CdS thin film synthesis, on glass substrate in alkaline condition. In this study they have developed the deposition of PbS-CdS bilayers in the temperature range from 30 to 80^0C. J. Puiso et al [108] studied the growth of lead sulphide thin film on (100) Si, and (111) Si crystalline substrate by successive ionic layer adsorption and reaction, technique (SILAR), at room temperature.

The effect of thickness on thermoelectric properties of PbS thin films was studied by E.I. Rogacheva et al [109]. Lead sulphide layer's were prepared by thermal evaporation of PbS in vacuum and deposition onto (001) KCl substrate at 570 K, covered with EuS layer. R.R. Hawaldar et al [110] presented a communication on self-assembly of nanocrystalline lead sulphide at liquids -liquid interface. The average particle size of the PbS nanocrystals calculated from the half width of (220) and (400) peaks using Scherrer's formula is 5nm. The band gap is of the order of 18eV as reported by them.

Synthesis, opto-electro-structural studies on the thin films of lead chalcogenides were done by Sushil Kumar et al [111]. X-ray diffraction

technique, optical absorption and current-voltage characteristics of PbS, PbSe, PbTe were used to characterize the films Schottky junctions of PbS, and PbTe with indium metal were made. The barrier heights of these junctions have been determined having the values 0.25, 0.28, 0.27 eV respectively. Sehgaier et al [112] prepared the lead sulphide films by using lead nitrate, sodium hydroxide and thiourea as precursors at different dipping times at constant room temperature. The grain size as a function of lead nitrate concentration was calculated from both XRD and SEM which showed good agreement.

K.P. Kalyanikutty et al [113] reported XRD, SEM, and HREM analysis of ZnS and PbS ultra thin films formed at the organic-aqueous interface. The effect of hydrazine hydrate on the photoconductivity of nano structured sulphide thin films was reported by M. Sasani Ghamsari et al [114]. The chemical deposition of PbS films was done on glass, quartz, sapphire and $SrTiO_3$ substrate. The number of trapping centers in the deposited PbS was increased by the presence of hydrazine hydrate into chemical deposition bath.

Polycrystalline thin films of lead sulphide grown by using substrate colloidal chemical bath depositions were reported by F.A. Fernandez-Lima *et al* [115].Changes in morphology, composition, grain-size and thickness were characterized by RBS, XPS and AFM techniques. All samples maintained 1:1 stoichiometry.

Lead sulphide nanoparticles were deposited by Dan Li *et al* [116]. Lead sulphide thin films were used in solar photovoltaic applications cubic lead sulphide thin film on TCO glass substrate was deposited by galvanic technique was reported by Anup Mondal and Nillohit Mukherjee [117]. Nano particles of lead sulphides were deposited by Amalnerkar *et al* [118] by liquid-liquid interface reaction technique.

Lead sulphide nano particle growth on glass, quartz and silicon substrates was achieved by Joshi *et al* [119]. Larramend *et al* [120] has studied the effect of surface on photosensitivity on chemically deposited PbS thin films. Valenzuela-Jauregui *et al* [121] studied optical properties of chemically deposited PbS thin films. For deposition purposes lead acetate, thiourea and

triethanolamine was used. The alkaline conditions were maintained by addition of 1M sodium hydroxide. Ichimura *et al* [122] have prepared lead sulphide thin films in aqueous solutions by photochemical reactions. The reaction bath contained lead acetate & sodium thiosulphate. The deposition was carried out in acidic condition by using H_2SO_4.

1.6.3 Literature Search of $Cd_xPb_{1-x}S$ thin films

Kepi Wu and J. N. Zemel [123] have grown $Cd_xPb_{1-x}S$ epitaxial films on heated cleaved or polished NaCl substrates. The optical transmission and reflection were measured from 2000 Å to 40 μ. There was a systematic increase in the energy of the fundamental absorption edge as x increased. Films were 1.5–6 μ in thickness

Vilmos Rakovics [124] investigated the Chemical bath deposition of nanocrystalline CdS and CdPbS layers and studied their photoconductivity. The CdS layers was characterized using X-ray diffraction, scanning electron microscopy, optical absorption, DC electrical conductivity, photoconductivity measurements $Cd_xPb_{1-x}S$ ($0 \leq x \leq 1$) thin films were prepared on glass substrates using the chemical bath deposition method by E. Pentia et al [125]. The structural, electrical, and photoelectrical properties of the films were investigated, and all were dependent on the x value. The experimental results point toward possible ternary deposition in limited composition ranges (near pure PbS or CdS) whereas, for the rest, the deposited film is rather a mixture of phases [not $Cd_xPb_{1-x}S$ but $(CdS)_x(PbS)_{1-x}$]. Sanjeev Kumar and B Bhattacharya [126] prepared the material of configuration ($Cd_{1-x}Pb_xS$) by precipitate technique in methanol with $x = 0.2, 0.4, 0.6, 0.8$. The films of this material were deposited by the vacuum deposition method. Spectroscopic technique has been used for the band gap determination. It has been found that the band gap decreases with increase in Pb concentration. L.P. Deshmukh *et al* [127] have reported PEC applications of chemically deposited $(CdS)_x(PbS)_{1-x}$ thin films.

1.7 The Research Problem

The chalcogenide films of II-IV, IV-VI and II-IV-VI families have already emerged as the potential candidates of high performance and low

production cost [128-130]. High optical absorption coefficients and nearly matching band gaps are the root courses for their popularity. With suitable choice of material composition many of the electrical, optical and structural properties could be controlled smoothly and thus optimized to a described level.

Now a days cadmium lead sulphide are considered as efficient absorbers in visible region of solar spectrum, and application of these films in solar energy conversion systems seems to be a promising field for research. Thus taking the practical importance of cadmium lead and sulphide into account, it was decided to prepare $Cd_xPb_{1-x}S$ thin films by simple chemical bath deposition method and to study the effect of different preparative parameters. The various preparative parameters like pH, temperature, deposition time, concentration of solution and speed of rotation will be optimized to obtain good quality thin films. The films obtained of varying composition 'x' will be characterized by using XRD, atomic absorption, electrical conductivity measurements, optical absorption measurements, thermoelectric power measurements and scanning electron micrograph techniques. The mechanism of film growth was also studied.

The different parameters like activation energy, crystallite size, stoichimetry, band gap, type of optical transition, type of semiconductor and thickness will be determined from measurements. The PEC cell properties will be determined by depositing films on conducting stainless steel substrate. For the fabrication of PEC cell thin film will be used as semiconductor electrode and graphite as counter electrode. The solvent for PEC cell will be sulphide and polysulphide. The performance of cell will be observed by measuring various cell parameters like capacitance-voltage, current-voltage, barrier height and power output curves.

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