CHAPTER - I

Introduction

1.1 Energy Considerations

The ‘energy’ has acquired significant importance in the recent years due to worldwide energy crisis that is being intensified by the depletion of conventional fossil fuels. This crisis is observed because of increased demands of energy by ever increasing population and modernization of world. 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]. Today’s climate of growing energy needs and increasing environmental concern has forced the scientists to find an efficient alternative to replace the existing non-renewable and pollution causing fossil fuels. The demands may be fulfilled by number of alternative energy sources such as nuclear, thermal, hydroelectric, wind etc. Among these sources, some are costlier, time consuming and depleting with fast rate, while some are intermittent and depend on the whim of nature. Today, every country draws its energy needs from a variety of sources through commercial as well as non-commercial methods. During the past several decades, the energy demands of the world have continued to increase at an annual rate of 3 to 4% due to increase in population, transportation, increasing standard of living and industrialization.

The environmental restrictions are being made more stringent all over the world. This might be helpful in using pollution free and risk free energy technologies. Serious concerns are being made recently towards developing the feasible cost effective technology based on the use of plentiful available solar energy. It is believed that the solar energy will fulfill the world’s future energy needs with minimum adverse
environmental consequences. The problem is how to harness the energy obtained from the sun efficiently and effectively.

Solar energy is the energy produced directly by the sun and collected elsewhere, normally on the earth. The sun creates its energy through a thermonuclear process that converts about 650,000,000 tons of hydrogen to electromagnetic radiation including ultra-violet, visible, infrared streams out into space in all direction [3]. Only a small fraction of the total radiations produced reach the earth which is the indirect source of nearly every type of energy used today. Even fossil fuels owe their origins to the sun. They were once living plants and animals whose life was dependent upon the sun.

Much of the world’s required energy can be supplied directly by solar power. Due to nature of solar energy; two components are required to have a functional solar energy generator. These two components are a collector and a storage unit. The collector simply collects the radiation that falls on it and converts a fraction of it to other forms of energy (either electricity and heat or heat alone). The storage unit is required because of the non-constant nature of solar energy. At certain times only a very small amount of radiation will be received at night. The storage unit can hold the excess energy produced during the periods of maximum productivity and release it when the productivity drops.

The amount of solar energy reaching the earth’s surface is about 8,000 times than that of total commercial energy used. For a nation like India, which has a long duration of summer, the harnessing of the sun’s energy could be the best alternative. Now a day’s thin film solar energy conversion devices have become important and are eco-friendly for non conventional alternative sources of energy. The present research is being focused on trapping the solar energy. Recently, for harvesting solar energy the development of low cost flat panel solar cells, thin film devices, concentrator system and many innovative concepts are much in progress.
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The major task remained behind is to convert sunlight directly into electrical energy effectively. At present, there is a need to convert solar energy into electrical energy without contamination of environment.

1.2 Thin Film Technology

Thin films are two dimensional micro materials which are obtained by one of the established technique such as physical vapor deposition, chemical vapor deposition, electrochemical deposition, arrested precipitation etc. By using any one of these technique, thin films of the order few nm to few μm thick can be obtained on a variety of surfaces (substrates) like metals, ceramics, insulators, plastic etc. The basic steps involved in thin film deposition are creation of material to be deposited in atomic, molecular, particulate or ionic form at specific rate, transport of created materials to the substrate and deposition of film by nucleation and growth process. By knowing deposition steps and techniques one can get, the film of desired property by proper modifications in deposition steps.

Thin film solar panels are one of the means of generating electric power from the sun. They include most modern amorphous silicon photovoltaic cells, which are not rigid, unlike traditional panels. These thin panels could end up by replacing rigid mono-crystalline and polycrystalline solar cell.

1.3 Solar Energy

The term solar energy means energy from the sun in form of heat and light. It refers to the utilization of the radiant energy from the sun. The Sun delivers $1.2 \times 10^{14}$ kW (i.e $4.32 \times 10^{20}$ J/h) energy to the earth, which is about 10,000 times more than the present energy consumption [4]. The energy that the Earth receives from the Sun in just one hour is equal to the total amount of energy consumed by humans in one year [4]. About 30% of the radiated light is reflected back to the space while the rest are absorbed by cloud, ocean and land masses [5]. Solar radiation spectrum (figure 1.1), describes the visible and near-visible radiation emitted from
the sun. Their wavelength range within the broadband range of 0.20 to 4.0 μm describes the different regions. Infrared radiation emitted from the atmosphere is termed as terrestrial radiation. Components of solar and terrestrial radiation and their approximate wavelength ranges are shown as follows:

Ultraviolet: 0.20 - 0.39 μm
Visible: 0.39 - 0.78 μm
Near-Infrared: 0.78 - 4.00 μm
Infrared: 4.00 - 100.00 μm

Approximately 99% of solar or short wave radiation reaching at the earth's surface is contained in the region from 0.3 to 3.0 μm while most of terrestrial, or long-wave, radiation is contained in the region from 3.5 to 50 μm.

Figure 1.1 Solar radiation spectrum
Figure 1.2 Electromagnetic Spectrum

The sunlight has to travel through the atmosphere under clear sky condition is very important because it determines the solar radiance. This distance is the shortest when the sun is at the zenith, i.e. directly overhead. The ratio of an actual path length of the sunlight to this minimal distance is known as the optical air mass. When the sun is at its zenith, the optical air mass is unity and the radiation is described as air mass one (AM1) radiation. It is the standard value to measure solar cell performances [4]. The energy received from the sun in form of light (photons) is then converted into electricity by the process called photovoltaic technology (PV).

Solar energy is one of the most promising and non conventional energy sources. The future of solar power development will depend on how one deal with a number of serious constraints associated with it, including scientific and technological problems, marketing and financial limitations, political and legislative actions. The electromagnetic spectral range of solar radiations is 2000-20,000Å. Approximately, half of this spectral energy is distributed in the visible region. However, energy of these radiations reaching the earth’s surface is reduced considerably due to atmospheric
extinction, absorption by the gases, humidity, scattering due to clouds, dust etc. Only recently considerable attention has been paid for the large scale utilization of solar energy because of its relative abundance and the apparent minimal adverse environmental effects of its conversion [6-9]. The main areas of interest are solar thermal conversion, photovoltaic conversion, bioconversion etc. In solar thermal energy conversion, the heat from the thermal collector is used to run heat engines for the generation of electricity. Photovoltaic is a direct energy conversion process and ideally efficient. Its feasibility has been demonstrated in small systems for special applications both on ground and in space [6,10]. For the photovoltaic energy conversion on large scale, this study has been undertaken in detail. Cost comparison with other energy systems shows that the photovoltaic conversion system is uneconomical. The higher cost for such solar cells is one of the reasons. The cost associated with these cells can be reduced significantly with progress in technology [11].

There are various methods of trapping solar energy for useful applications. Mainly solar energy can be harnessed by photovoltaic cells and photo electrochemical (PEC) cells. In photovoltaic cells, the maximum portion of radiation is directly converted into electricity. The conversion device is called solar cell. A solar cell is essentially a p–n junction in solid state between dissimilar semiconductors [11].

Semiconductor based photo-electrochemical (PEC) cell forms one of the chemical route for trapping solar energy. In PEC cell, the junction formation is easier (mere dipping of the semiconductor in the electrolyte) as compared to the p-n junction formation in solid state photovoltaic cells. A large number of semiconductors of the mixed oxide and chalcogenide types have been studies for their PEC performance. The semiconductor-electrolyte (S-L) junction is attracting a great deal of interest due to many advantages over the conventional solid-solid (S-S) p–n junction such as easy set up of the device and use of semiconductor other than costly
silicon. The energy conversion efficiency of PEC cell so far achieved is about 20 % [12].

A low cost photovoltaic cell is a thin film cell that has a price competitive with traditional fossil fuels and nuclear power energy sources. This includes second and third generation photovoltaic cells. Thin film technologies reduce the amount of material required in creating a solar cell. Although this reduces material cost, it may also reduce energy conversion efficiency too.

1.4 Historical Survey of Solar Cells

Solar cell converts light radiation directly into electrical energy by means of photovoltaic effect. The photovoltaic effect is the generation of an electromotive force by the absorption of ionizing radiation [13]. This photovoltaic effect can occur in many systems such as: semiconductor–semiconductor junction, semiconductor-metal junction, semi-conductor–liquid junction, etc. The generation of electron-hole pair inside the semiconductor is possible only when, the energy of incident photon is greater than that of the band gap energy of the semiconductor. If this excess photo-generated electron-hole pairs are separated by an energy barrier system, an electromotive force is developed. If this electron is allowed to pass through the external circuitry a photocurrent will flow. Among these three types of junctions we will confine our attention towards the photovoltaic effect at semiconductor-liquid junction. In the last decade interest in photo-electrochemistry itself has blossomed due to the pioneering work of Gerischer [14,15].

Application of this knowledge to energy conversion was first shown by Fujishima et.al [16] by demonstrating the photo-decomposition of water at TiO₂ electrodes illuminated with ultraviolet energy radiation. This information and their subsequent work [17-19] played key impression on the number of research groups around the world working in this field. Gerischer [20] proposed the use of electrochemical photovoltaic (ECPV)
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cells for solar to electrical conversion using reversible redox system as an electrolyte. From the last 10-15 years remarkable progress has been made in the direction of conversion of optical to electrical and chemical energy via electrochemical photovoltaic cell. A great deal of work in this area by many workers [21-30] summarizes the findings.

Although conversion of optical energy into electrical energy by the use of photovoltaic effect is a well-known phenomenon [31-34]. The reduction in cost has been a great hindrance in recent years in order to provide an economically competitive source of electricity. One of the ways in achieving the low cost solar cell goal is the development of thin film technologies for photovoltaic. Direct band gap of semiconducting materials having high absorption coefficient and high quantum yield are found suitable for this purpose. In this respect II-VI compounds meet these requirements as they are direct band gap materials and can be made available in thin film form [35-38]. Among these, cadmium sulphide is the most challenging semiconductor whose band gap is 2.4 eV and absorption coefficient is of the order of $10^4$-$10^5$ cm$^{-1}$. It has received considerable attention in recent years due to its potential applications in semiconductor – liquid junction cells [39-42] as well as in CdS/Cu$_2$S solar cells [43-46]. Electrochemical photovoltaic cells consisting of n-CdS photoelectrode and different electrolytes, with 5% efficiency are reported [20,47]. CdS films prepared by various techniques such as vacuum evaporation, chemical bath deposition and spray pyrolysis have been used in the ECPV cells with configuration CdS/NaOH-S-Na$_2$S/C or Pt and their results are reported [48,49]. However, optical conversion efficiency of these cells is low as compared to single crystal cells. The efficiency of these cells depend mainly on semiconducting photo-electrode, redox electrolyte and the counter electrode material. Ellis et.al. [50] showed that a sulphide/polysulphide redox couple gives good fit to photoanode made of the polycrystalline CdS thin film. However, the sulphide/polysulphide redox couple suffer from drawbacks, such as susceptibility to oxidation under
exposure to atmosphere and high absorption of incident light in solution state [51,52]. This can be eliminated by using back wall illumination. Different counter electrode materials have been electrochemically tested by Allen and Hickling [53]. Platinum has been found to be electrochemically inert material for use as a counter electrode in ECPV cells. A study by Hodes et al [54] showed that the efficiency of graphite (treated in CoS or NiS) was comparable to Pt or even better.

The quality of the photo-electrode plays a stringent part in improving the efficiency of ECPV cells. Incorporation of various dopants [55-57] in semiconductor lattice, heat treatments in different ambient conditions [48,58] and surface modification techniques have been tried to modify the film properties suitable for electrochemical photovoltaic applications.

1.5 Solar Energy Conversion

The basic idea of a solar cell is to convert light energy into electrical energy. The energy of light is transmitted by photons, small packets or quantum of light. Electrical energy is stored in electromagnetic fields, which in turn can make a current of electrons flow. Thus a solar cell converts light i.e. a flow of photons, to electric current i.e. to a flow of electrons.

When photons are absorbed by matter in the solar cell, their energy is used to excite electrons from low energy to higher energy states where the electrons can move more freely. The perhaps most well-known example of this is the photoelectric effect, where photons give enough energy to electrons in a metal to escape the surface. In an ordinary material, if the electrons are not given enough energy to escape, they would soon relax back to their ground states. A solar cell however prevents this from happening. The electrons are instead forced to one side of the solar cell, where the build-up of negative charge allows a current flow through an external circuit. The current ends up at the other side (or terminal) of the
solar cell, where the electrons once again enter the ground state, as they have lost energy in the external circuit.

The photovoltaic (PV) systems convert light energy into electricity. The term "photo" is a stem from the Greek "phos," which means "light." "Volt" is named after Alessandro Volta (1745-1827), a pioneer in the study of electricity. "Photo-voltaics" then, could literally mean "light-electricity". PV systems are already an important part of our lives. The simplest solar systems power many of the small calculators and wrist watches that we use every day. More complicated systems are used to provide electricity for pumping water, powering communications equipment, and even lighting our homes and running our appliances. PV power is the cheapest form of electricity for performing these tasks.

The movement of light from one location to another can best be described as though it were a wave and different types of radiation are characterized by their individual wavelengths. These wavelengths indicate radiation with different amounts of energy. The longer the wavelength, the lesser the energy, for example the red light has a longer wavelength with less energy than violet light. At each second, the sun releases an enormous amount of radiant energy into the solar system. The earth receives a tiny fraction of this energy, an average of 1367 watts (W) square meter (m²) of the outer edge of the earth's atmosphere. The atmosphere absorbs and reflects some of this radiation including most X-rays and ultraviolet rays. Still, the amount of sunshine energy that hits the surface of the earth every minute is greater than the total amount of energy that the world's human population consumes. The earth's atmosphere and cloud cover absorb, reflect and scatter some of the solar radiation entering the atmosphere.

1.6 Photovoltaic Technology

Photovoltaic is the direct conversion of solar radiation into electricity. Photovoltaic (PV) literally means 'light-electricity'. This
technology is feasible with advanced semiconductor devices and with the main areas of applications being terrestrial and space [59]. Photovoltaic as an energy technology has numerous environmental benefits. As domestic source of electricity [59], it contributes to the nation’s energy security. It is reliable and needs little maintenance. However, its major drawback is the high cost when compared to other electricity sources [60]. Some materials exhibit a property known as the photoelectric effect that causes them to absorb photons of light and release charge carriers (electrons and holes). When these free electrons are collected, electric current results. Solar cells are built using this effect. Incident photons which enter the lattice of solar cell structure have a small but definite null probability to create an electron-hole pair. In fact, if their energy (hu) is greater than the energy band-gap (Eg) of the material used in the solar cell (h is the Planck constant and the frequency is ν = c/λ, with c is the speed of light and λ the wavelength), then they have enough energy to break covalent bonds that tie valence electrons to the nucleus of the single atom. Further more this break results in the movement of electrons over the lattice in the valence band of energy [59,60].

Basically, photovoltaic effect consist of three processes namely, generation of charge carriers due to the absorption of photons in the materials that form a junction, separation of the photo-generated charge carriers in the junction and the collection of the photo-generated charge carriers at the terminals of the junction. Figure 1.2 below shows the structure and working principles of solar cells. When photons strike a photovoltaic cell, they may be reflected, pass right through, or be absorbed depending on the energy, band-gap and the wavelength of these photons. However, only the absorbed photons provide energy to generate electricity. When a semiconductor material is exposed to sunlight, energy is absorbed and this leads to the creation of electron-hole pairs. The negatively charged electrons are displaced from their parent atom and are collected at the front contact with holes left behind. These results in imbalance of charge
between the material's front and back contact hence, creating a voltage potential. When the contacts are connected to external load, then electricity flows [61]. However, because of the limitations in output voltages, (approximately 0.5V) and currents (approximately 7A) of individual cells[59], the overall output power is low and may not support adequately the intended load. In order to increase the output power, cells are connected together in series and parallel to obtain higher voltages and currents in a packaged weather-tight module. The photovoltaic cell efficiency is higher than the module efficiency unless the cells are identical electrically. Moreover, modules can further be connected to form an array. Array refers to the entire generating plant, irrespective of the number of integrated modules which is largely dependent on the amount of power output needed.

The first practical use of solar cells was the generation of electricity on the orbiting satellite Vanguard-1 in 1958 made from single crystal silicon wafers. This solar cell had efficiency of 6% [62]. This solar cell has become the first solar cells to be used for terrestrial generation of electricity. This eventually resulted in efforts at increasing its efficiency and lowering their price. The crystalline silicon solar cell technology has improved and it is the dominant solar cell technology today. Over the last few years, the PV industry has experienced a strong growth, which is expected to continue. As this technology has matured, cost has become increasingly dominated by material costs, namely those of the silicon wafer, the glass cover sheet and encapsulants. Crystalline silicon (c-Si) technology presently dominate the photovoltaic industry contributing more than 95% through the cells and modules based on mono- and multi crystalline wafer technology. However, the continuous increase in demand has made cost reduction a major challenging. Currently research effort is towards reducing the material cost by developing thin film technology.
1.7. Solar Cell Materials

The most important parts of a solar cell are the semiconductor layers, because this is where the electron current is created. There are a number of different materials suitable for making these semiconducting layers and each has benefits and drawbacks. Unfortunately, there is no one ideal material for all types of cells and applications. In addition to the semiconducting materials, solar cells consist of a top metallic grid or other electrical contact to collect electrons from the semiconductor and transfer them to the external load and a back contact layer to complete the electrical circuit. The complete cell is covered by a glass or other type of transparent encapsulant to seal the cell and keep weather out. An anti reflective coating can also be made to keep the cell from reflecting the light.

1.8. Types of Solar Cells

The solar cell converts light energy directly into electrical energy by means of the photovoltaic effect. The charge separation in semiconductor system due to incident ionizing radiation at the junction is called ‘built in potential’. This potential sweeps out the charge carriers as a result of absorption of incident photons. It results due to difference in the Fermi energy at the junction. Based on the nature of junction formed solar cells can be classified as:

(a) Silicon Solar Cells

Mono-crystalline silicon solar cells, polycrystalline silicon thin film solar cells and amorphous silicon thin film solar cells are the three important types. The highest conversion efficiency of silicon solar cells so far achieved in laboratory is 24.7%.

The large-scale applications and industrial production is still limited because of the high cost price of silicon. An alternative is to use polycrystalline silicon in the form of film. The polycrystalline silicon thin film solar cells are of relatively low cost and more efficient than
amorphous silicon thin film battery, the maximum conversion efficiency achieved was 18%.

(b) Multiple Compound Thin Film Solar Cells

Multiple layers of inorganic thin film materials, such as gallium arsenide, cadmium sulphide and copper indium selenide can be an efficient way to harness solar energy. The efficiency of CdS, CdTe polycrystalline thin film cell efficiency is more than amorphous silicon thin film solar cell efficiency.

Gallium arsenide solar cell shows the conversion efficiency up to 28%. GaAs compound materials have matchable band gap, higher absorption efficiency, anti-radiation ability. Moreover, it is not sensitive to heat and therefore highly suitable for manufacturing efficient single-junction cells. But the expensive Gallium and Arsenic material largely limited the popularity of using Ga As cells.

Copper indium selenide thin film battery (CIS) shows the same conversion efficiency as that of polycrystalline-silicon. It has low price, good performance and simple processings. The only problem is the source material as indium and selenium are relatively rare and costly.

(c) Multi-layer Polymer Solar Cells Modified Electrode

The use of organic polymers instead of inorganic materials is just the beginning of a solar cell manufacturing research. As the organic material is flexible and its cost and manufacture is easy, the large-scale use in solar energy conversion can provide cheap electricity production of solar energy. However, the parameters such as life of cell, efficiency of the battery, stability of the material needs to be further studied.

(d) Nano-Crystalline Solar Cells

Nano-crystalline TiO₂ solar cells chemical energy is a newly developed is cheap, simple process and has a stable performance. The optical efficiency is 10% more. The production cost of silicon solar cells is
only 1/5 and that of nanocrystalline TiO₂ is 1/10. Research and development of such batteries has just started in the near future it will gradually increase and come in the market.

1.9 Thin Film Deposition Techniques

Thin films play a dominant role in the all fields of science and technology. Thin films used are not only for technological applications but also for decorative purposes. Thin films vary in thickness from a few nm to a few microns. Thin films can be deposited by several techniques. For the sake of brevity, some of the techniques are classified as [63].

1.9.1 Physical Vapour Deposition Techniques.

In this technique, vapours are utilized in getting the deposits. Physical Vapour Deposition techniques are further classified as below.

1. Thermal Vacuum Evaporation

In this technique the source material is vaporized and the vapors are made to condense on a substrate, kept at certain temperature or elevated under vacuum. So the system consists of a vacuum chamber, deposition system, thickness monitor, substrate heater and holder.

2. Electron Beam Evaporation

In this technique, the concept is similar to that of thermal evaporation except that the heating is done by a beam of electrons.

3. Sputtering

There are different types of sputtering techniques:

DC sputtering
RF sputtering
Magnetron sputtering

In all cases the target of the material to be evaporated is bombarded with ions tearing the atoms from the target and deposition on the substrate.
4. **Hot Wall Vacuum Evaporation**

This is a variation of the vacuum evaporation technique; in vacuum evaporation, the evaporated species are deposited at all places inside the chamber in addition to the substrate. This results in loss of material. To avoid this loss, the vapor species is collimated through a hot wall and directed towards the substrate. The system is similar to the vacuum evaporation system, but has a wall heater whose temperature is equal to that of the source and a substrate heater.

5. **Molecular Beam Evaporation**

In this technique, films of mono-crystalline quality can be deposited. The process requires an ultra high vacuum environment. A very low growth rates are possible, moreover each monolayer can be characterized *in situ* and any deviation from the desired growth pattern can be corrected instantaneously. The deposition system consists of growth chamber, analytical chamber and transfer chamber.

6. **Pulse Laser Deposition**

The PLD method of thin film growth involves evaporation of a solid target in an ultra high vacuum chamber by means of short and high energy pulses. In a typical PLD process, a pulsed laser beam vaporizes the surface of the target and the vapor condenses on a substrate. The main components are a laser, optics and a vacuum system. This process is conceptually simple. A laser beam vaporizes a target surface producing a film with the same composition as the target. Versatile range materials can be deposited in a wide variety of gases over a broad range of gas pressures. High quality samples can be grown reliably in 10 to 15 minutes.

### 1.9.2 Chemical Vapour Deposition Techniques

Chemical Vapour Deposition techniques are further classified as below;

In this technique, chemicals (sources) containing deposition constituent are transported in vapor phase to the substrate where they react
to generate deposition. Sometimes reactants are not available in the gaseous phase. In such cases a carrier gas (usually hydrogen or argon) is bubbled through the liquid source which carries the source vapor to the substrate. These techniques form a sub-class of CVD technique and are called chemical transport processes. Chemical transport processes may be hydride process, halide process or organo-metallic process (MO-CVD). For example, to deposit epitaxial Si, one can either use a gaseous source of a silane SiH₄ which gets decomposed at the surface or liquid source of silane, silicon-tetra chloride, SiCl₄ bubbled by hydrogen gas. Hydrogen carries the SiCl₄ vapor and reacts with at the surface to generate Si. SiCl₄ process is actually preferred because it removes the metallic contaminants as well. Similarly, in halide process, for growth of GaAs, one can use liquid Ga, AsCl₃ source and hydrogen as the carrier gas. AsCl₃ saturated with hydrogen is made to flow over heated Ga region where AsCl₃ breaks into gaseous As and HCl. HCl reacts with Ga to generate gaseous Gallium chloride. Both of these reacts at the surface of the wafer, which is little cooler, to crystallize GaAs. In hydride process, gaseous Arsine, (AsH₃P) Phosphine (PH₃) etc, are used for group V element source. In MO-CVD, alkyl metal liquid source is used for group III elements with hydrogen as the carrier gas. Gaseous AsH₃/ PH₃ etc are used for V group element. The process can be broken down into many sub-steps-convection of gases, diffusion of reactants across the boundary layer, adsorption of reactants on the surface, several steps of chemical reactions at the surface, desorption of products and then diffusion out and convection of the products. The velocity of gas just on the surface is zero and increases steadily as we move away. Distance between surface and uniform velocity region is called boundary layer. Usually two of these, that is, diffusion across boundary layer and surface reaction are the most important rate limiting steps. Diffusion rate is nearly independent of temperature while, surface reaction rate goes as exp(-1/T) (exact logarithmic dependence is determined by the exact elementary rate determining chemical step). Hence at higher temperature,
the rate limiting step should be the diffusion and the rate should be pretty much independent of temperature. While at low temperatures, surface reaction is the rate limiting step.

In CVD systems growth varies a little bit along the length of the tube due to two reasons. One is that the boundary layer thickness varies with distance and other is simply because of the consumption of the gases with distance. First reason affects only diffusion limited processes but the second one affects both of these. For diffusion limited systems, this is countered by tilting the substrates a little bit. This reduces the tube cross-section and increases the flow. For the surface reaction limited processes, a simple temperature gradient is usually maintained to counter this problem.

Following are most popular CVD/PVE techniques;

1.9.2.1. Atmospheric Pressure CVD

In this case deposition usually is limited by the diffusion of reactants through the boundary layer. Therefore, it is important to maintain a constant gas concentration across all the wafers, as wafers needs to be placed flat next to each other in the tube. In AP/CVD systems, if one needs to deposit epitaxial layers, then one needs to go for higher temperature and hence it would be diffusion controlled. At lower temperatures, rate would be surface reaction limited and film will be polycrystalline.

1.9.2.2. Low Pressure CVD

In this case deposition rate is limited by the chemical reaction rate at the surface. This can be achieved by lowering the temperature. The deposition rate would be sensitive to temperature and therefore needs good temperature control. But reaction rates are not sensitive to the concentration (partial pressure) of the gases over the wafer assuming that the surface reaction controls the rate and hence diffusion always makes sufficient number of gas molecules available at all spatial location even though this number might not be uniform. If the pressure is kept same as
that with AP/CVD and temperature is lowered to get into surface reaction rate limited regime, the deposition rate would be much smaller, deteriorating the quality of film. Hence the total pressure of the gases is reduced keeping the partial pressure of reactants to be same. This speeds up the diffusion rate since there is much less collisions and hence diffusivity goes up. There is always a limit to what extent we can reduce the total pressure without reducing the partial pressures.

1.9.2.3. Plasma Enhanced CVD

This is used mainly when sufficient deposition rates are needed at low temperature.

1.9.3. Other Techniques

This method of deposition makes use of the fact that by controlling the rate of release of the ions and preventing the formation of a precipitate, thin films can be deposited on large area substrates. It includes;

1.9.3.1. Electro-deposition

This technique is based on the Faraday’s laws of electrolysis. It is a simple technique and the driving force is either the potential or current. In this technique, very large area films can be deposited and the process can be scaled up for commercial production. Variations of this technique are the electroless technique, pulse deposition technique and selective plating technique.

1.9.3.2. Spin Coating

Spin coating is the preferred method for application of thin and uniform films to flat substrates. The substrate is rotated at high speed in order to spread the fluid by centrifugal force. Rotation is continued for some time with fluid being spun off the edges of the substrate until the desired film thickness is achieved. The solvent is usually volatile, providing for its simultaneous evaporation.
1.9.3.3. Spray Pyrolysis

This technique is used for a thick film coating. The films of thicknesses in the range of 10 to 40 micrometers can be easily deposited by this method. In this technique, the material to be deposited is prepared in the powder form, then made into a paste and printed through a screen on to a substrate. This is further processed for obtaining the film.

1.9.3.4. Sol gel Coating

The sol-gel process allows synthesizing ceramic materials of high purity and homogeneity by means of preparation techniques different from the traditional process of fusion of oxides. This process occurs in liquid phase solution of organo-metallic precursors (Zr (IV)-Propoxide, Ti(IV)-Butoxide, etc.), which, by means of hydrolysis and condensation reactions, lead to the formation of a new phase (Sol). The Sol is made of solid particles of a diameter of few hundred of nm suspended in a liquid phase. Then the particles condense in a new phase (Gel) in which a solid macromolecules is immersed in a liquid phase (solvent). Drying of gels by means of low temperature treatments (25-100°C), it is possible to obtain porous solid matrices (Xerogels). The fundamental property of the sol-gel process is that it is possible to generate ceramic material at a temperature close to room temperature.

1.9.3.5. Chemical Bath Deposition (Solution Growth)

The film can be deposited on any suitable substrate by dipping it in appropriate solution of metal salt without use of electrical energy. The deposition may occur either by homogeneous or heterogeneous chemical reaction usually by reduction of metal ion in presence of reducing agent. Metallic compounds, and their alloys can be deposited using these techniques. In case of binary compounds of the II-VI group, the cations of the respective metal, complexed with suitable complexing agent is allowed to react with the source of chalcogenides ion. The cations and anions are allowed to generate slowly by increasing temperature of the reaction bath.
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The ions so produced combine on substrate via nucleation. Further growth of these nuclei takes place by absorbing more and more ions to get film. The growth usually takes place by ion-by-ion condensation method. Therefore this method is also called as solution growth, controlled/arrested precipitation and electroless plating.

1.10. Literature Survey

The wide-band gap II-VI semiconductor materials attract attention of many scientific and industrial researchers throughout the world. The extensive research of II-VI semiconductor materials was started in 1920 with the investigation of luminescence and optical properties of ZnS [64]. Although the application of II-VI semiconductors for LEDs is a main driving force for scientific research on these materials, the potential of these materials was found to be much broader. It was realized that the materials of this group pose such a broad range of bandgaps that they are capable of absorbing/ emitting nearly every color in the visible light spectrum. If the ternary II-II-VI compounds are included, the range of band gaps becomes even more continuous. So that their properties can be tuned to make them applicable in the field of solar energy harnessing, X-ray detectors, photo-resistors, electron beam screens, etc [65].

Zinc Telluride (ZnTe), is one of the binary compounds belonging to II-VI group semiconductor materials, Zinc telluride is a chemical compound with the formula ZnTe. This material is an intrinsic semiconductor material with band gap of 2.23 - 2.25 eV. It is usually a p-type semiconductor. Its crystal structure is cubic, like that for sphalerite, with lattice constant 0.61034 nm. In bulk form, it has the appearance of grey to brownish-red powder or ruby-red (crystals) when refined by sublimation while in film form it looks to be whitish with yellow tint. Zinc telluride can also be prepared as hexagonal crystals. Zinc telluride has attracted a great deal of attention due to their proven material properties. The energy position corresponds to the maximum sensitivity of the human
eye and therefore makes ZnTe an appealing material for green LED production [66].

ZnTe is important for development of various semiconductor devices, such as blue LEDs including multi-junction solar cells [67]. It can be used for solar cells as a background layer and the p-type semiconductor in PIN structure. Zinc telluride together with lithium niobate is often used for generation of pulsed terahertz radiation in time-domain terahertz spectroscopy and terahertz imaging. When a crystal of such material is subjected to a high-intensity light pulse of sub-pico second duration, it emits a pulse of terahertz frequency through a nonlinear optical process. Conversely, subjecting a zinc telluride crystal to terahertz radiation causes it to show optical birefringence and change the polarization of a transmitting light, making it a terahertz detector [68]. Zinc telluride can be easily doped and for this reasons it is one of the more common semiconducting materials used in making optoelectronic devices [69-71]. Vanadium-doped zinc telluride, ZnTe:V, is a non-linear optical photorefractive material of possible use in the protection of sensors at visible wavelengths in holographic interferometry, reconfigurable optical interconnections, in laser optical phase conjugation devices and as all-optical laser digitizers [72]. Doped ZnTe offers superior photorefractive performance at wavelengths between 600-1300 nm in comparison with other III-V and II-VI compound semiconductors. By adding manganese as an additional dopant (ZnTe:V:Mn) its photorefractive yield can be significantly increased.

In modern material engineering, not only the high quality of the fabricated material is important, but also the flexibility, effectiveness, and moderate expense of the production method is employed. ZnTe thin films due to wide applications in the field of microelectronics and optoelectronics are extensively studied for electrical, optical and structural properties. Several deposition techniques for thin-films of ZnTe
preparation were found. Some of them are vacuum deposition [73], molecular beam epitaxy (MBE) [74], metal organic vapor phase epitaxy (MOVPE) [75], metal organic chemical vapor deposition (MOCVD) [76] and electrochemical deposition [77]. The chemical bath deposition (CBD) method has been emerged largely as a low cost, convenient technique for large area deposition of semiconductor thin film material on conducting/nonconducting substrate. The method does not require sophisticated instrumentation and is useful for deposition even at low temperature. CBD is an aqueous analogue of chemical vapor deposition (CVD). The constituent ions are dissolved in a water solution, and the thin films are produced through a heterogeneous surface reaction. CBD is capable of producing nano, microcrystalline, or even epitaxial thin films [78]. Zinc telluride thin films have been deposited by Murali et al [79] using brush plating technique on conducting glass and titanium substrates at different temperatures (30-90 °C). The films were polycrystalline in nature with peaks corresponding to the cubic phase. A direct band gap of 2.30 eV was observed. XPS study indicated the formation of ZnTe with a uniform distribution of Zn and Te throughout the entire thickness.

The structural, optical and electrical properties of ZnTe thin films deposited electrochemically from a citric acid aqueous solution containing ZnSO₄, TeO₂ onto Au-coated Cu substrates have been investigated by Ishizaki et al [80]. The results of resistivity and optical absorption measurement demonstrated respectively. As the Zn concentration in the electrolyte was reduced over the range of 5-50 m mol dm⁻³, the resistivity of the films continuously found to decrease while the band gap was found to be increased. Quantitative analysis of energy dispersive x-ray analysis and inductively coupled plasma study indicated that the composition ratio (Zn:Te) was approximately stoichiometric under all conditions. X-ray diffraction results revealed that all the ZnTe thin films obtained showed a preferred (111) orientation with cubic structure. The conduction activation energy was 0.33 eV.
A study on the crystalline structure and morphology of vacuum evaporated ZnTe thin films has been made by Rusu et al [81] using X-ray diffraction technique and atomic force microscopy. The optical bandgap determined from absorption spectra (supposing allowed direct band-to-band transitions) varied between 1.95 eV and 2.40 eV. The films studied showed polycrystalline nature with zinc blende structure. The film crystallites are preferentially oriented with (111) planes parallel to the substrates XRD patterns and AFM images have been used to determine the microstructural parameters.

Atomic force microscopic characterization of ZnTe epitaxial films with different thicknesses were investigated by Klapetek et al [82]. The AFM study enabled them to determine the values of the mean grain size, grain size distribution, root mean square values of the heights of the irregularities and the distribution of the directions of the normals. It was shown that the values of these quantities can best describe the morphology of the ZnTe film surfaces in a sufficient way. Further, it was shown that the structure of the surfaces of the ZnTe films exhibit facets forming a grain structure with a strong slope anisotropy and that the linear dimensions of the grains varies linearly with thicknesses of the ZnTe films.

The photoelectrochemical applications of ZnTe obtained by using a single-step electrodeposition process from an aqueous salt solution have been studied by Mahalingam et al [83]. The structure was found to be cubic and the degree of crystallinity increased with decreasing deposition potential. The surface morphology reveals uniform grain size for films deposited at more negative deposition potentials (−1.1 V versus the SCE). The p-type semiconducting materials endowed with acceptable stability and compatibility are required so that enhanced photo-responsiveness to illumination may become possible. The photo-potential of annealed photo-electrode was larger which can be attributed to an increase in grain size of annealed ZnTe samples.
Mazumdar et al [84] studied the photoconductivity of thermally evaporated p-type ZnTe thin films at elevated temperatures. A gap type cell configuration with Al electrodes on glass substrates was used. The conductivity was found to obey two distinct conduction mechanisms within the region of applied fields. The low field photoconduction was ohmic while at high fields it was Poole-Frenkel type. With increase of ambient temperatures, the Poole-Frenkel conductivity regions were found to extend to lower fields. The temperature dependence of dark conductivity also was found to be of similar nature. The observations support the process of neutralization of localized charges in the depletion regions in the grain boundary potential barriers due to the presence of both thermally generated carriers and photo-generated carriers in the studied ZnTe thin film samples.

Preparation of ZnTe thin films and indium doped ZnTe films using thermal evaporation method have been carried out successfully by Patter et al [85]. XRD characteristics revealed that ZnTe thin films became crystalline after doping and annealing at 150°C. The morphology of the films as studied by AFM supports the XRD results. Optical band gap of the doped films was decreased with increase in doping concentrations, A two order of magnitude enhancement in the conductivity of the doped films was observed.

Islam et al [86] electrodeposited ZnTe layers as window materials in ZnTe/CdTe/CdHgTe multi-layer solar cells using a low-cost electrodeposition method. The deposited layers mainly consist of ZnTe phases. p-type ZnTe window materials having bandgap 2.10-2.20 ev have been used in CdTe based solar cell structures following new designs of graded bandgap multi-layer solar cells. The structures of FTO/ZnTe/CdTe/metal and FTO/ZnTe/CdTe/CdHgTe/metal have been investigated.

The cubic ZnTe with small grains clustering form spherical agglomerates with varying sizes up to ~300 nm. The ZnTe film has been
used as a window layer for solar cells of the type, FTO/ZnTe/CdTe/metal and FTO/ZnTe/CdTe/CMT/metal. The 525 mV Voc was found for initial studies on FTO/ZnTe/CdTe/ metal structures. Work is progressing to improve PV parameters of this type of structures.

Strain effect and atomic arrangement studies in ZnTe/GaAs lattice-mismatched hetero-structures have been carried out by Lee et al [87] The Transmission electron microscopy (TEM) measurements were performed to investigate the lattice mismatch and the micro-structural properties of a ZnTe layer grown on a GaAs (100) substrate. The results of the TEM images and the electron direction patterns showed that there was a large lattice mismatch between the ZnTe epitaxial layer and the GaAs substrate and that 60% and 90% dislocations together with stacking faults, were observed near the ZnTe/GaAs hetero-interface.

Investigation of ZnTe homoepitaxial layers grown by metal organic vapour phase epitaxy on VGF grown (100) ZnTe:P wafers have been carried out by Traversa et al [88]. The epilayer crystalline quality was strongly improved by increasing the wafer insitu annealing temperature from 190°C to 240°C in agreement with a previous SIMS analysis indicating that annealing temperatures > 240°C are necessary to reduce most native oxides from the wafer surface however annealing beyond 350 °C generates defects in the epilayer (most likely close to the pi layer/substrate interface) during the growth.

Oxygen-doped ZnTe phosphors for synchrotron x-ray imaging detectors were successfully prepared by a dry synthesis process using gaseous doping and etching media [89]. The emission intensity of dry O2-doped samples was three times more intense than from ZnO-doped samples, indicate that ZnTe:O is a promising phosphor candidate for synchrotron X-ray imaging applications.

Single crystal films of ZnSe and ZnTe are frequently employed in various branches of applied research and industry. For example, they are
used to create optical waveguides on the basis of a three-layer ZnSe/ZnTe/ZnSe system prepared on single-crystal GaAs substrate. These films are also employed in many applications in optoelectronic and integrated optics. Both the ZnTe and ZnSe films utilized for these purposes must exhibit high optical quality. Therefore efficient optical methods must be used to check this quality. Franta et al [90] studied the spectral dependences of the optical constants, i.e. the refractive index and extinction coefficient, of the epitaxial thin films of ZnTe and ZnSe prepared by MBE onto single crystal GaAs substrates within the spectral region 220-850 nm respectively. The multi-sample modification of the optical combined method based on the simultaneous interpretation of the experimental data corresponding to VASE and NNSR was used for this purpose. These physical models used to calculate the theoretical values of the ellipsometric quantities and reflectance have been described.

The absorption and transmission of ZnTe thin films have been measured at wavelengths of 0.32-2.3 μm by Pal et al [91]. The optical constants \( n, K \) were measured in this range, although the short wavelength refractive index \( n \) measurement was limited by the band gap. The abnormal decrease of refractive index near the band gap is correlated with the effects of film thickness and doping with impurities like In, PbCl\(_2\), BaF. It has been observed that there is an increase in optical band gap with decrease in crystallite size, increase in strain and decrease in lattice constant value.

The influence of substrate temperature on microcrystalline structure and optical properties of ZnTe thin films deposited onto well-cleaned glass substrates by vacuum evaporation have been investigated [92]. The crystalline nature of the film increases with increase in the substrate temperature while the transmission was found to decrease with increase of substrate temperature and thickness. The optical band gap energy showed an inverse dependence on substrate temperature and thickness. ZnTe due
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to its wide direct band gap has been extensively studied for application as back contact for CdTe in CdTe/CdS heterojunction solar cells. The transport mechanism in these crystalline films under a.c. fields was studied in the frequency range 12 Hz to 100 kHz, at different temperatures (303-483K) showed dependence of capacitance and loss factor on frequency [93]. The process of a.c. conduction has been explained on the basis of hopping conduction mechanism.

ZnTe semiconductor films have been evolved by Ishizaki et al [94] from a citric acid solution. Although the solubility of Te species in acid solution is quite low the author observed a relatively higher solubility of Te species at pH=4 using a citric acid electrolytes. The electro-deposition of stoichiometric ZnTe from the citric acid electrolytes took place at potentials positive to the Nernst potential for bulk-Zn deposition and negative to that for bulk-Te just as with sulfate acidic electrolytes. The deposits appear reddish-brown with granular and compact morphology. The surface coverage is almost complete and the grains visible in the photograph represent aggregates of very small crystallites.

Bhatti et al [95] deposited solar cell grade ZnTe thin films onto thoroughly cleaned glass substrates kept at room temperature by vacuum evaporation of $\approx 10^{-4}$ torr. These films were annealed at temperatures of 100$^\circ$C, 200$^\circ$C, 300$^\circ$C and 375$^\circ$C for 15 minutes in air atmosphere. The optical properties of as evaporated and annealed films were then studied. A slight rise in band gap energy was observed. The films obtained were without pinholes and very well adherent with the glass substrate. The variation of band gap (2.15-2.26 eV) has been attributed to the grain growth and improvement in the crystalline nature of the films caused by annealing.

There has been much interest in synthesis and physical characterization of II–VI family semiconductors. Most studies in this field were focused on cadmium chalcogenides and zinc chalcogenides [96-99].
However, owing to the toxicity problem of mercurides, reports about mercury chalcogenides are scarce. Conventional methods for preparation of mercury chalcogenides include solid-state reaction [100], reaction of metal cation with hydrogen chalcogenides in aqueous solution [101] and molecular precursor methods [102]. Solid-state reaction usually required elevated reaction temperature and the reaction was not easily controllable. For reaction of metal cation with Hg₂Te in aqueous solution, although the processing temperature is low, the hydrogen chalcogenides are gaseous (at standard temperature and pressure) and are highly toxic. As for molecular precursor methods, they usually involve the formation and thermal decomposition process of a complicated organometallic compound, using organometallic reagents and compounds containing an R–E bond as precursors. Though this method needed relatively lower temperature than solid-state reaction and was expected to be a very mild route to form metal chalcogenides, obtaining the vapor phase precursor of organometallic compounds is very difficult. Kulifay [103] has described a preparative method of HgSe from HgO and Se, which needed a two-step reaction with HgSeO₃ as the intermediate. The method however excludes toxic Hg and organometallic reagents. Many scientists are still exploring new, safe, simple route to grow II–VI semiconductors with the goals of lowering processing temperature, avoiding complex organometallic reactions toxic precursors, and searching for milder preparation conditions. It is known that mercury will react with sulfur at room temperature [104]. However, elemental reaction at room temperature to produce HgSe or HgTe is not reported. Recently, a liquid ammonia route has been used to synthesize metal chalcogenides at room temperature [105]. But in this method, very toxic metal mercury was employed and the obtained HgS was amorphous, which needed post heat treatment at 250°C–300°C.

An oxide direct-conversion route for the formation of nanocrystalline HgS, HgSe and HgTe at room temperature in ethylene diamine is presented by Y Li et al [106]. Solvent ethylene diamine is found
to have a very important role in the electron-transfer process of the whole reaction. The mercury oxide was used as mercury source and tellurium as chalcogenides source. The obtained products were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS) techniques. (XRD) patterns showed that the product of HgTe was cubic (zinc blende structure).

The EC-ALE is the electrochemical analogue of atomic layer epitaxy (ALE) and atomic layer deposition (ALD), all of which are based on the growth of materials as a monolayer at a time, using surface limited reactions. EC-ALE involves the successive application of electrochemical surface limited reactions such as under potential deposition (UPD) to form the desired material in a series of steps, a cycle to produce a monolayer of the material. The number of such cycles then determines the thickness of the resulting deposit. Deposition of HgTe by electrochemical atomic layer epitaxy (EC-ALE) in order to optimize an EC-ALE cycle for the growth of better quality HgTe have been carried out by Venkatasamy [107]. The best deposits with thickness 71.9 nm were formed using Hg and Te deposition potentials of 0.40 V and -0.35 V respectively and using a Te stripping potential of -0.70 V. Electron probe microanalysis (EPMA) of the deposit indicated a Te/Hg atomic ratio of 1.02. X-ray diffraction studies showed the deposits to grow in a strongly (111) orientation. Room temperature IR absorption studies of HgTe indicated a negative bandgap of -0.20 eV.

Surface and electronic structure characterization of electrochemically deposited HgTe nanocrystalline thin films have been carried out by Rath et al [108]. The AFM study as a function of the film thickness showed an increase in film roughness and thickness. The scaling exponents such as roughness exponent and growth exponent, associated with the film growth are found to be 0.88±0.05 and 0.21±0.04 respectively. The shifting of the valence and core levels to higher binding energy as
evidenced by XPS suggest the change in electronic structure of the nano-
HgTe films possibly due to the surface roughness.

Colloidal HgTe nanocrystals with widely tunable narrow band gap
energies are quite useful in fields ranging from telecommunications to
molecular vibrations for the visible and the near-IR[109] spectral region. A
multitude of highly luminescent wide-gap semiconductor nanocrystals
(NCs) have been chemically synthesized. Despite the enormous success of
colloidal NCs used, for example, in lasers [110] as fluorescent markers in
biological systems or in a single photon source [111], the development of
NCs with tunable IR emission up to wavelengths of more than 3 \( \mu \)m is still
challenging [112]. Hg chalcogenides are most appropriate to obtain narrow
band gaps from NCs in the quantum confinement regime because their
bulk constituents exhibit zero band gaps whereas those of all alternative
binary narrow gap semiconductor such as lead chalcogenides and group III
antimonides are at least 0.18 eV (InSb, 300 K) [113]. So far, the best
synthetic routes to Hg chalcogenide NCs are those based on thiol-capping
in aqueous medium [114-115]. The optical characterization of NCs in
aqueous solutions is, however, restricted to the near-IR due to the
opaqueness of water at wavelength >1.3\( \mu \)m. Synthetic approaches to HgTe
NCs [116] in the organic solvents suffered from the high reactivity,
instability and tendency to uncontrolled growth even at temperatures as
low as 70-100\(^{\circ}\)C.

Kovalenko [117] synthesized HgTe in aqueous solutions and
transferred them to organic solvents by a ligand-exchange procedure. By
the choice of the stabilizer we optimized the growth dynamics, the
luminescence quantum yields (up to 40\%) and the phase transferability. As
a result we obtain stable HgTe NCs giving room temperature emission
which is strongly size-tunable between the wavelength of 1.2 and 3.7 \( \mu \)m.
The HgTe were prepared in aqueous solutions via a room temperature
reaction between Hg(\( \text{ClO}_4 \))\(_2\) and \( \text{H}_2\text{Te} \) gas (bubbled through) in the
presence of the hydrophilic thiols, thioglycerol (TG), thioglycolic acid (TGA), L-cysteine, mercaptoethanol (ME), and mercaptoethylamine (MEA) as stabilizers.

Rath et al [118] recently electrochemically deposited HgTe with crystallite size of 7 nanometers. The author observed visible luminescence; these unusual optical properties are considered to be due to larger quantum size effect as Bohrs excitation radius for HgTe is around 40 nm. The bandgap observed was 2.14 eV as against the negative bulk value (-0.15 eV).

In recent years, the II–VI family of compound semiconductors, namely cadmium telluride (CdTe), zinc telluride (ZnTe) and mercury telluride (HgTe) has been the focus of great interest due to their low cost and high absorption coefficients for applications in photo-voltaic and photo-electrochemical cells [119-120]. The film technology is the base for development of modern microelectronic devices. In particular, the semiconductor films are used in the solar energy conversion systems for the signal guidance in optical transmission lines. As stated earlier, Zinc telluride (ZnTe) is a direct gap semiconductor (2.25 eV bandgap energy), it exhibit p type conductivity due to the high degree of self-compensation. It is a potential candidate for photovoltaics. Another member is HgTe, which is a semi-metal with n type, high carrier concentration. The ever increasing technological needs for micro and optoelectronic devices such as light emitting diodes (LEDs) and photodetectors, operating in the spectral regions from visible to far-infrared continues to attract much of the current research activities on the thin films of different wide-gap and narrow-band semiconductor heterostructures and compounds [121-123]. Among II-VI based hetero-structures with potential applications to the realization of efficient photo-detector, many efforts have been focused on heterostructures based on popularly known ternary solid solution Cd$_x$Hg$_{1-x}$Te (0<x<1) thin films as well as bulk materials [124-126]. The
compounds of IIA-VIB group (e.g. CdTe, HgTe, ZnTe) are very promising materials for use in optoelectronic and high-temperature electronic devices. Ternary alloys of II-VI compounds are potential candidates for the detection of electromagnetic radiation. The solid solutions composed of a mixture of a wide bandgap II-VI compound with the semimetal HgTe may be "tuned" to yield semiconductors with a band gap that vanishes at an intermediate alloy composition. Recently, ternary compounds have received much attention in the field of solar cells owing to their interesting properties of band gap and lattice constant modulation by composition variation [127-128]. Mercury zinc telluride (HgZnTe,) is an alloy of mercury telluride and zinc telluride having a wide range of band gap tunability between 0 eV and 2.25 eV. It offers potential advantages over Cd based HgCdTe, HgCdSe due to its high stability [129]. The alloying makes it possible to obtain narrow-gap semiconductors for the fabrication of infrared/visible photon detectors. Among this group, Hg₁₋ₓCdₓTe is the most extensively studied alloy system because it has proved to be useful as a material for high performance photoconductive and photovoltaic infrared [130]. At present, the CdHgTe is the variable bandgap system mostly used in the fabrication of infrared (IR) photodetectors [131]. However, in spite of the achievements in material and device quality, difficulties still exist due to the instability of the Hg₁₋ₓCdₓTe alloys. The existence of certain problems related to the use of CdHgTe, in particular, the instability of its lattice, surface, and interphase boundary have initiated the development of alternative materials for applications [132]. ZnHgTe seems to occupy a prominent place over CdHgTe due to improved structural properties (such as micro-hardness and dislocation-formation energy) and fairly high mobilities of charge carriers and they have been extensively studied both theoretically and experimentally [133-134]. Most recently, Sher et al [121] have shown from theoretical considerations that the weak HgTe bond is destabilized by alloying it with CdTe, but is stabilized by ZnTe. Similar to a CdHgTe, ZnHgTe alloys form
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a continuous series of solid solutions [135]. The composition and temperature dependences of the band gap in these materials are similar to those in CdHgTe [68]. It seems that new narrow-gap semi-conductors based on Hg will gradually replace CdHgTe, especially in applications where stringent requirements are imposed on the stability of a device’s parameters [136]. This type of alloy offer composition based modulation of semiconductor properties such as electrical, band gap, lattice constant etc. ZnHgTe alloy attracts special interest over other cadmium based alloys due to following reasons: (i) the bond between Hg and Te is shorter and stronger than Cd and Te offering additional stability. ii) The use of ZnTe as a host lattice is less destabilizing than use of CdTe, providing an additional lattice stability to alloy system [137] (iii) Zn1-xHgxTe films exhibit better coefficient of absorption, (vi) the micro-hardness of ZnHgTe based alloy is higher than CdHgTe based alloy [138]

The growth and characterization of Hg1-xZnxTe, a new narrow-gap semiconductor in single crystals formed for the first time have been reported by Sher et al [121]. The single crystals were grown by liquid phase epitaxy (LPE) on (111) oriented CdTe substrate using the open tube slider boat method. Solutions of Hg in Te were equilibrated with excess polycrystalline ZnTe for approximately two hours. Growth temperature was around 500°C. Epilayers of Hg0.87Zn0.13Te and Hg0.77Zn0.23 Te were obtained by controlling the proportion of Hg in the Te solution. The composition of the layers was determined by the x-ray fluorescence method with lattice constant data measured by an x-ray diffractometer. A lattice constant of 6.405 Å for x = 0.16 and 6.385Å for x = 0.23 have been reported. These results fit very well with those expected from Vegard’s law. The characteristics of the epilayers were found to be similar to those obtained for p-type Hg1-xCd1xTe samples.

The ZnHgTe occupy a prominent place among these materials as it has a number of advantages that have been extensively studied and include,
most importantly, improved structural properties (such as microhardness and dislocation-formation energy) and fairly high mobilities of charge carriers. The composition and temperature dependence of the band gap in this material is similar to those in CdHgTe. The ZnHgTe system is however exhibiting large segregation coefficients with higher melting temperatures of the corresponding binary compounds. At the same time, epitaxial methods of growth (in comparison with the growth of bulk crystals) make it possible to obtain large-area epitaxial layers and complex multilayer structures at relatively low temperatures which is especially important for the attainment of good operating characteristics in the next generation of photovoltaic and MIS devices [136,139].

In addition to analysis of the dependences of the band gap and lattice constant on the alloy composition, it is necessary to take into account the fact that the majority of alloys are unstable in a certain range of compositions. An alloy in the instability region tends to experience a decrease in its free energy as a result of decomposition, i.e., a phase transformation that brings about a disruption in the macroscopic homogeneity of crystals and the formation of a mixture of phases with differing compositions. When decomposition occurs without the formation of nuclei of new phases, it is referred to as spinodal decomposition. The corresponding phase-diagram curve that separates the domain of alloy compositions of that are unstable with respect even to negligible fluctuations is referred to as the spinodal curve [140]. Unordered semiconductor alloys exhibit a positive enthalpy of mixing, which leads to a decomposition that counteracts the stabilizing effect of internal stresses. The conduction and valence band offsets at the interface between two semiconductors can be controlled using the corresponding strains which make it possible to obtain improved heterostructure based devices. The strain also ensures an additional degree of freedom when fitting the energy-band structure to experimental data and varying the optical and kinetic properties of semiconductors. Strains and stresses in materials grown by
epitaxial methods such as molecular-beam epitaxy and the deposition of metal–organic chemical compounds from a vapor phase are mainly caused by a mismatch between the lattices of the epitaxial layer and the substrate. The presence of elastic relaxation in thin films also affects the phase transformations and stability [141]. The thermodynamic stability of the alloys under consideration has not as yet been adequately studied. Owing to the miscibility gap, one cannot obtain alloys based on II–VI compounds containing an arbitrary composition of components. For example, in Cd_{1-x}Hg_xTe and Zn_xHg_{1-x}Te systems with a slight lattice-constant mismatch, the critical temperature of decomposition is comparatively low, which makes it possible to obtain a more or less regular alloy in the entire range of compositions under normal growth conditions [142]. At the same time, a fairly wide region of phase separation (0.35 < x < 1) has been experimentally observed [143] for only bulk Mn_xHg_{1-x}Te alloy.

As stated earlier, these systems are studied rather extensively in recent years, both experimentally and theoretically [139,144-145]. Like Cd_{1-x}Hg_xTe system, Zn_xHg_{1-x}Te alloys form a continuous series of solid solutions [142]. However, the internal local strains arising as a result of mixing of two components (ZnTe and HgTe) with unmatched lattice constants (lattice mismatch ~ 6%) lead to a larger asymmetry of the spinodal-decomposition curves with respect to x = 0.5 and to an increase in the critical temperature. In particular, according to Deİbuk et al [146], Tc = 457 K at x = 0.53, which is in good agreement with the results reported by Patrick et al. [144] (Tc = 455 K at x = 0.56). Therefore, it is possible to obtain a continuous series of solid solutions at typical growth temperatures. As the film thickness decreases, the biaxial stresses originating in the substrate affect the shape of the decomposition curves more and more. In particular, the critical temperature of decomposition decreases slightly and the spinodal-decomposition region shifts to higher zinc concentrations. These results thermodynamically account for the higher quality of epitaxial Zn_xHg_{1-x}Te films grown on Cd_{0.8}Zn_{0.2}Te substrate as compared to that of
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films grown on CdTe substrates and are consistent with the experimental data [76,139].

So far the Hg$_{1-x}$Cd$_x$Te system has been extensively studied due to similarity in the lattice parameters of HgTe and CdTe that facilitates the material growth process. The development of improved techniques for better control of crystallinity and homogeneity has contributed to the success of using Hg$_{1-x}$Cd$_x$Te for infra red detectors over a wide spectral range. Bulk crystals of Hg$_{1-x}$Zn$_x$Te have been grown by R. Triboulet et al [125] by the travelling heater method using tellurium as a solvent. This material was found to have a higher hardness than Hg$_{1-x}$Cd$_x$Te. The higher bonding strength in Hg$_{1-x}$Zn$_x$Te has prompted further investigations on the epitaxial growth and properties.

Epitaxial Hg$_{1-x}$Zn$_x$Te films with properties comparable to high quality Hg$_{1-x}$Cd$_x$Te of the same cut-off frequency have also been grown on GaAs substrates by molecular beam epitaxy [147]. The deposition of Hg$_{1-x}$Zn$_x$Te films by MOCVD is considered as complicated due to (i) the large difference in reactivity and stability of HgTe and ZnTe, and (ii) the high partial pressure of Hg over Hg$_{1-x}$Zn$_x$Te [148]. Therefore, the deposition of Hg$_{1-x}$Zn$_x$Te films should be carried out at low temperatures to minimize the dissociation of Hg$_{1-x}$Zn$_x$Te.

The optical transmittance and reflectance have been measured for thin films of Zn$_x$Hg$_{1-x}$Te by M.C. Petty et al [149]. Values for the energy gaps as estimated from the position of the absorption edge show that the system is a ‘zero-gap’ alloy similar to CdHgTe. A rigorous evaluation of the absorption coefficient has been made for compositions in the range 0>x>0.4. Calculations for direct transitions assuming a zero-gap system, gave results that were in good agreement with measured experimental values, for absorption coefficients less than 5000 cm$^{-1}$. For values larger than 5000 cm$^{-1}$ the agreement between theory and experiment is better if the effects of higher bands on the E-k relationship of the conduction band
are also taken into account. An anomalous shift in the absorption curves after annealing in Ar is found and thought to be due to stress relief within the film. The electrical measurements by Cuceanu et al [150] on bulk Zn$_x$Hg$_{1-x}$Te and Petty and Juhasz [149] on thin films of this material suggest that the band structure of this alloy is similar to that of Cd$_x$Hg$_{1-x}$Te [151] with the ‘zero-gap’ composition at about x = 0.06. Thero et al [152] report the electrodeposition of mercury zinc telluride Hg$_x$Zn$_{1-x}$Te thin films of composition varying between x = 0 to x = 0.4 on indium tin oxide (ITO)/glass substrates. The films were found to be smooth, uniform and adherent with a small grain size (0.1-0.9 μm). X-ray diffraction analysis of the films indicated a shift in the (111) peak with alloying in good agreement with a Vegard's law behavior. The optical absorption edge was found to be a soft, direct band edge with optical absorption coefficients of the order 10$^4$ cm$^{-1}$.

The narrow-gap II–VI and IV–VI alloys are convenient objects for studying the electron–phonon interaction. However, the concentration of free carriers in the IV–VI alloys is rather high (∼10$^{18}$ cm$^{-3}$) which complicates the study of this effect by the optical reflection method. The concentration of free carriers in the narrow-gap Hg$_{1-x}$Zn$_x$Te alloys is considerably lower (∼10$^{16}$ cm$^{-3}$). Therefore, the plasma component exerts less effect on the lattice reflection spectrum. Using the dispersion analysis and the Kramers-Kronig method, the frequencies of the transverse optical (TO) phonons of the HgTe-like and ZnTe-like modes have been determined depending on the compositions [153]. The temperature dependency of the frequencies of the Te phonons and the damping parameter were measured for the narrow-gap alloy with x = 0.1 in the range of 80–200 K. A decrease in the frequency of the TO phonon of the soft mode in the vicinity of the inversion point of the bands at T = 110 K was found for the first time by optical methods. The damping parameter slightly increases in the vicinity of this temperature. The result obtained qualitatively agreed with the theoretical model. The band structure of the
HgZnTe alloys was found to be similar to that of the well-studied HgCdTe alloys [119]. The ZnTe binary compound is a wide-gap semiconductor and the HgTe compound is a semiconductor. After the band inversion, a HgZnTe alloy becomes a semimetal. All three bands intersect at an inversion point. Sher et al[121] found that the zero-gap state for the alloy with \( x = 0.1 \) is attained at \( T=120 \, \text{K} \). By varying the temperature gradually in the vicinity of this point, it is possible to pass the band-inversion point. A decrease in the frequency of the transverse optical (TO) phonon near the band-inversion point due to the electron–phonon interaction was theoretically predicted for the narrow-gap IV-VI alloys. According to the model suggested, deformation, caused by optical mode splits the levels almost degenerate at the inversion point and the energy gap widens. A decrease in energy of the electron system due to a decrease in the energy of valence-band electrons is compensated by an increase in elastic energy of the lattice which causes softening of the corresponding phonon mode.

The solidus temperatures of the pseudo-binary phase diagram for several compositions in the low \( x \) region were measured by differential thermal analysis and the HgTe-ZnTe pseudobinary phase diagram was constructed [154]. The densities of two HgZnTe melts, \( x = 0.10 \) and 0.16 were determined by an \textit{in situ} pycnometric technique in a transparent furnace over temperature range of 110°C and 50°C respectively. The thermodynamic properties of the melts such as the heat capacity and enthalpy of mixing were calculated for temperatures between the liquids and 1500°C. The \( (0 \leq x \leq 1) \) solid solutions have been studied extensively in the low \( x \) region \( (x \leq 0.2) \) as a potentially superior material for the IR detector applications because the chemical bonding makes the material relatively more stable compared to HgCdTe.

Polycrystalline ZnHgTe thin films were successfully synthesized from acidic solution baths using electro-deposition in the galvanostatic mode [119]. The preparation of stoichiometric films could be achieved by
appropriate selection of the growth parameters. However annealing of electrodeposited films at high temperature is required for the improvement of crystallinity of the films. Optical absorption studies revealed a direct band gap and a band gap tailoring is observed with the change of Hg content in the films. The electrical resistivity of the films is found to decrease with increase in the Hg content in the films.

To date, a number of growth techniques in particular, molecular beam epitaxy (MBE) and liquid-phase epitaxy (LPE) have been employed to grow different structures based on II-VI materials [155-157].

1.11. Scope of the Problem

In the recent years due to worldwide energy crisis that is being intensified by the depletion of conventional fossil fuels. This crisis is observed because of increased demands of energy by ever increasing population and modernization of world. The demand may be fulfilled by number of alternative energy sources such as nuclear, thermal, hydroelectric, wind etc. Among these sources, some are costlier, time consuming and depleting with fast rate, while some are intermittent and depend on the whim of nature. Today, every country draws its energy needs from a variety of sources through commercial methods.

It is believed that the solar energy will fulfill the world’s future energy needs with minimum adverse environmental consequences. The problem is how to harness the energy obtained from the sun efficiency and effectively. The semiconductor compounds of II-VI family including Cadmium telluride (CdTe), Zinc telluride (ZnTe), Mercury telluride (HgTe) and Mercury Selenide (HgSe) has been the focus of great interest due to their low cost and high absorption coefficients for applications to photovoltaic and photo-electrochemical cells (28,77). The pseudo-binary or ternary chalcogenide semiconductor thin films have been potential candidates for the detection of electromagnetic radiations. Zinc mercury telluride has a solid solution, has a wide range of band gaps tenability
between 0 to 2.25 eV. It offers potential advantages over cadmium based HgCdTe, HgCdSe, due to its high stability. The pseudo-binary material synthesized under controlled conditions offer composition dependent physical, electrical, optical, microscopic and structural characteristics suitable for photovoltaic applications.

In the present investigation, we attempted the deposition of Zn$_{1-x}$Hg$_x$Te pseudo-binary thin films on conducting (steel plates) as well as non-conducting (glass) substrate with the composition parameter (x) varying from zero to one. The systematic studies have also been made to characterize the material, to investigate their properties and to find it’s suitability for solar energy conversion. The various preparative parameters such as temperature, pH, concentrations of ions, rate of addition and rate of stirring etc has been finalized to get good quality thin films. Thin film photoelectrical properties, power output curves; Barrier height determination junction ideality factors have been studied, so as to optimize a good composition. The prepared material has been characterized by using the techniques such as XRD, AAS, SEM, electrical, thermo-electrical and photo-electrochemical properties are measured.

A ternary Zn$_{1-x}$Hg$_x$Te thin films are semiconductors of the type II-VI group. They are considered as a potential candidate for IR detection and solar cell applications because of manipulability of its band gap, higher absorption coefficient, stable ‘n’ type nature and wide spectral sensitivity ZnHg and ZnTe can be engineered better for application purpose suitably choosing the composition parameter x. Therefore for the proposed research work we plan to deposit and characterize Zn$_{1-x}$Hg$_x$Te thin films which accounts the practical importance of ‘Hg’ and ZnTe in general and of Zn$_{1-x}$Hg$_x$Te thin films will be prepared by simple chemical bath deposition technique. The deposition conditions like temperature, deposition time, pH of solution, speed of rotation will be optimized to obtain good quality thin film materials. The growth mechanism and kinetics will also be studied.
Electrochemical properties are studied by using conducting material like stainless steel. The photo-electrochemical (PEC) cells will be constructed by using thin film photo-electrode and suitable solvent. The cell performance will be studied in terms of various cell parameters like capacitance-voltage, current voltage, barrier height determination and power output curve.
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References

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