

SYNTHESIS AND CHARACTERIZATION CZTS THIN FILM SOLAR CELL

Submitted in partial fulfillment of the requirements for the award of
Master of Science Degree in Physics

By

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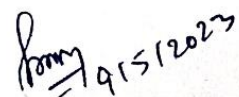
This is to certify that this Project report is the bonafide work of **KEERTHANA PRIYA G (41590010)** who have done the Project work as team who carried out the project entitled "**SYNTHESIS AND CHARACTERIZATION CZTS THIN FILM SOLAR CELL**" under my / our supervision from NOV 2022 to MAY2022.

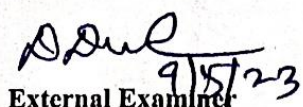

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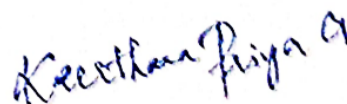

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DECLARATION

I KEERTHANA PRIYA G (Reg.No:41590010) hereby declare that the Project Report entitled **SYNTHESIS AND CHARACTERIZATION CZTS THIN FILM SOLAR CELL** done by me under the guidance of Dr. J. Anita Lett (Internal) and Dr T S Shyju (external) at SATHYABAMA INSTITUTE OF SCIENCE AND TECHNOLOGY, CHENNAI is submitted in partial fulfillment of the requirements for the award of Master of Science degree in Physics.

DATE: 09-05-2023

PLACE: Chennai



SIGNATURE OF THE CANDIDATE

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Abstract

Solar cells and solar-based products are one of the most rapidly growing industries on the earth today. Solar cells made primarily of silicon, are widely utilised all over the world. Thin-film solar panels, which have a thickness ranging from nanometers to one micrometre, are considered second-generation solar cells. The goal of this project is to develop thin-film solar cells on glass substrates in order to promote low-cost, environmentally friendly, and long-lasting solar energy devices. So, we choose II-VI group semiconducting materials that are selected for their wide-band-gap. These materials have good structural, optical, and electrical properties. Cadmium Sulphide (CdS) and Copper Zinc Tin Selenide (CZTS) is one among these groups. CdS thin film is a suitable n-type semiconductor for a window layer. CZTS is a p-type material is synthesized by mechanosynthesis at different milling time in the ratio of 2:1:1:4. The above mentioned semi conducting materials were thermally evaporated on a glass substrate at Room Temperature (RT) and various temperatures. For effective solar radiation absorption, Copper Zinc Tin Selenide (CZTS) is coated for a further increment of efficiency since it has a good transparent layer that absorbs more solar radiation and passed to the n-type material. The Structure of prepared CZTS nanocrystals is determined by XRD. The Absorbance and the transmittance of the CZTS Nanocrystals is calculated from the result of UV - DRS. The Electrical Properties were determined from the result of Hall Effect.

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List of abbreviation

CIGS - Copper Indium
GalliumCdTe - Cadmium
Telluride
CZTS - Copper Zinc Tin
Sulphide PVD - Physical
Vapour Deposition IAD - Ion
Assisted Deposition
IBS - Ion Beam Sputtering

PLD - Pulsed Vapour
Deposition MBE - Molecular
Beam Epitaxy CVD -
Chemical Vapour Deposition
CBD - Chemical Bath
Deposition CdS - Cadmium
Sulphide
FTO - Fluorine Tin
Oxide XRD - X-ray
Diffraction
JCPDS - Joint Committee on Powder Diffraction
Standards CIGS - Copper Indium Gallium Selenide
CdTe - Cadmium
Telluride GAAS -
Gallium Arsenide

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CHAPTER 1

INTRODUCTION

Any major gap in the flow of energy resources to an economy is referred as an energy crisis or lack of energy. In literature, it frequently refers to one of the energy sources employed in a specific time and location, particularly those that fuel industrial development and population growth, which have recently resulted in a rise in the need for energy on a global scale.

The world's energy requirements are rapidly increasing as a result of population growth and technological improvements. In order to meet future energy demand, it is crucial to choose a sustainable energy source that is dependable, affordable, and long lasting. In addition to other renewable energy resources, solar energy has a potential and cost-free energy resource that can be used to address long-term energy crisis concerns. Because of the tremendous demand for energy and the fact that the primary energy source, fossil fuel, is finite and expensive, the solar sector is expanding steadily on a global scale (Dhakal et al., 2014).

Since it has become affordable as a result of long, intensive research done to hasten its development, it has evolved into a tool to improve the economic position of developing countries and to support the lives of numerous impoverished people.

Considering that solar energy is better than other renewable energy sources in terms of availability, affordability, accessibility, capacity and efficiency, it would definitely be the best option for meeting future energy demand. Therefore, in order to overcome the energy crisis, the solar industry has the potential application and barriers for the better future.

1.1. THE SOLAR CELL

French physicist Edmond Becquerel was the first to experimentally prove the existence of the photovoltaic effect. He created the first solid state photovoltaic cell by creating the junctions by covering the semiconductor selenium with a thin layer of gold. The system's efficiency was only about 1%.

1.2. THE INITIAL PHOTOVOLTAIC SETUP

Becquerel built the first photovoltaic cell in his father's lab in 1839 when he was just 19 years old. In this experiment, the platinum electrodes were coated with silver chloride or silver bromide; once the electrodes were lighted, voltage and current were produced. The "Becquereleffect" is another name for the photovoltaic effect as a result of this research.

The next significant development in solar cell technology occurred in 1940, as it was discovered that when silicon samples with cracks in the middle were exposed to light, current flowed through the samples. As a result, one side was positively doped while the other side was negatively doped. This crack, which had likely occurred when the sample was created, really defined the boundary between regions holding different degrees of impurities. An electric field is produced when excess positive charge accumulates on one side of the p-n junction and excess negative charge accumulates on the opposite side. An incoming photon can kick-start an electron and cause current to flow when the cell is connected to a circuit

The original attempts to commercialise silicon solar cells failed miserably because they were expensive to manufacture.

Today, solar cells are found in a wide range of gadgets, including rooftop solar panels and pocket calculators. Research and development are ongoing with the aim of lowering the cost and increasing the efficiency to make solar power more competitive with fossil fuels. Better designs and sophisticated materials have made it possible to manufacture solar cells that reach above 40% efficiency.



Fig 1.1: The first silicon solar cell

1.3. THE SOLAR APPLICATION

When solar cells were proposed and launched on the Vanguard spacecraft in 1958, they were employed for the first time in a notable application as a backup power source for the main battery power source (Aldakov et al., 2013). The mission period might be increased by adding cells to the exterior of the body without significantly altering the spacecraft or its power systems.

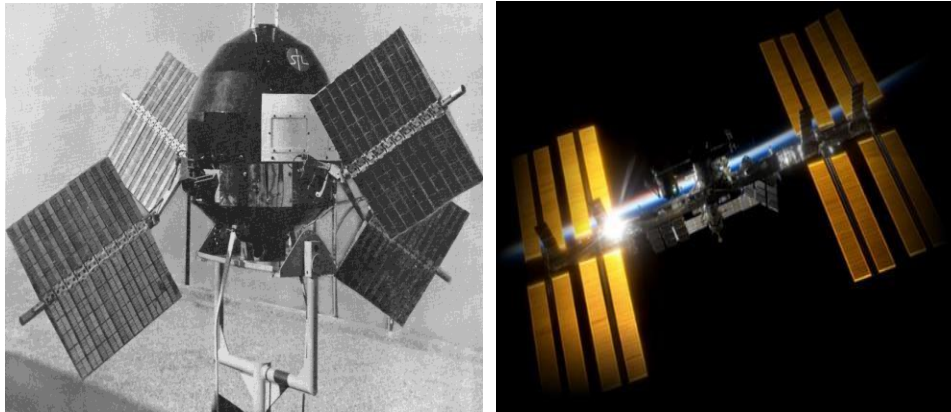


Fig1.2: Solar application in space

When spacecraft applications shifted to III-V semiconductor materials based on gallium arsenide in the early 1990s, they diverged from the silicon technology used for terrestrial panels. This led to the development of the current III-V multijunction photovoltaic cell used on spacecraft.

We need to know how much input power the photovoltaic receives in order to figure out the efficiency of the solar cell (Yin et al., 2013). Considering that we are familiar of the sun's luminosity (3.828×10^{26} W) and its distance from the Earth ($1\text{AU} = 1.496 \times 10^{11}\text{m}$) we may compute approximately

1.4. GENERATIONS OF SOLAR CELLS

1.4.1. First generation solar cell:

It is one of the most widely used technique that relies on silicon p-n semiconductor junction cells, which was demonstrated by Chaplin, Fuller, and Pearson first at bell labs in 1954. The market has dominated by silicon-based solar cells which is classified into monocrystalline, polycrystalline, and amorphous. The price can be exorbitant due

to lengthy payback period and high energy demands involved in silicon purification(Freitas et al., 2013).

For instance, the space industry uses high -grade single crystal cells, whereas amorphous silicon is used in low-power, affordable consumer devices. Despite being less effective, polycrystalline silicon is still employed due to lower manufacturing costs. The recombination characteristics of grain boundaries means that these cells are vulnerable to reduced efficiency. The cost is influenced by more than just crystal growth.

These cells must be packaged and placed, which are expensive. Group III/IV hetero-junction photovoltaic cells are used in industries like global arena where the efficiency is prioritized above cost. In comparison to silicon, a thickness of 100 μm is needed for 90% absorption whereas GaAs only needs thickness of 1 μm to obtain the same absorption.

GaAs seems to be a narrow band gap semiconductor, hence stimulation of an electron doesn't need a phonon help to transfer momentum, which is the fundamental cause of this. Furthermore, efforts are being made to create ribbon silicon whose goal is to cut production cost further, but this time by avoiding the slicing of crystal alloys.

Several various methods of producing ribbon silicon have been investigated and some are even currently at the trial scheme stage.

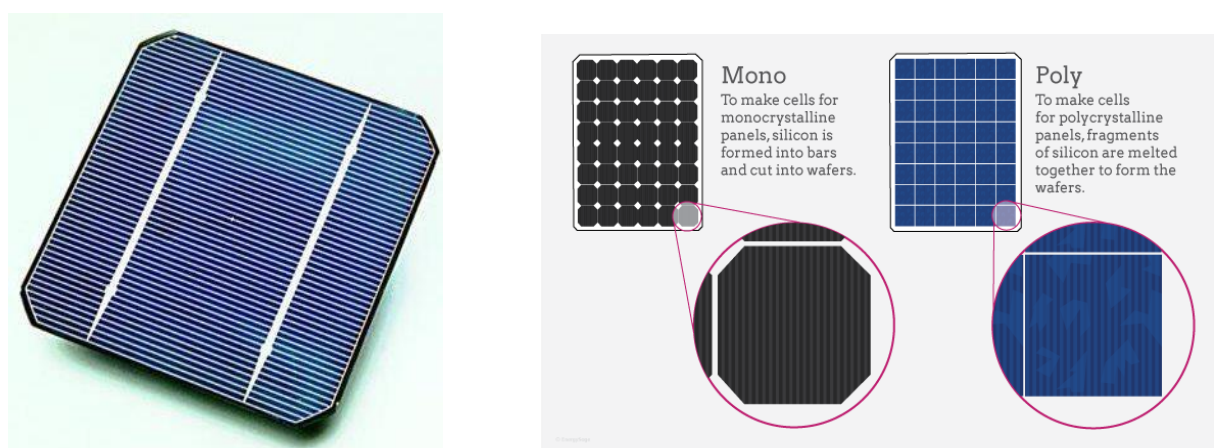


Fig 1.3: First generation solar cell

1.4.2. Second generation solar cell:

❖ Chalcogenides:

In the 1970s, second generation solar cells first appeared. The p-n heterojunction is produced by coupling copper indium Di selenide (CuInSe_2) and cadmium telluride (CdTe) with n-type cadmium selenide (CdS).

CdS is used as a window to p-n junctions because of its wide band gap (2.4 eV). Unlike first generation silicon cells which require a thick layer (100 μm), narrow band gap semiconductors only need a thin coating (10 μm) to completely absorb light. Quite apart from the positive test result for CuInSe_2 cells, a thorough understanding of these tertiary compound semiconductors is still required. Since they are ternary, the requisite manufacturing procedures are complicated especially when scaling up. Furthermore, the efficiency of employing rare elements like indium is under consideration. CdTe , on the other hand, is feasible as thin film and has solar energy pairing absorption spectrum which has a band gap of 1.5 eV. Thus, photons with energies more than 1.5 eV will be deposited and transformed into electrons (Wada et al., 2012).



Fig 1.4: Second generation solar cell

❖ Types of Thin-Film solar cell:

- a) Copper Indium Gallium Selenide (CIGS)
- b) Copper Zinc Tin Sulphide (CZTS)
- c) Cadmium Telluride (CdTe)

d) Copper indium selenium (CIS)

a) **Copper indium gallium selenide (CIGS):**

A thin-film solar cell used to turn sunlight into electricity is called a copper indium gallium selenide solar cell. It is created by coating a glass or plastic backing with a thin layer of copper indium gallium selenide solution, together with electrodes on the front and back to capture electricity. The material needs a considerably thinner coating than other semiconductor materials since it strongly absorbs sunlight and has a high absorption coefficient. Copper, indium, gallium, and selenium are the main components of the I-III-VI₂ compound semiconductor material known as CIGS. The semiconductor has a chalcopyrite crystal structure and is tetrahedrally linked.

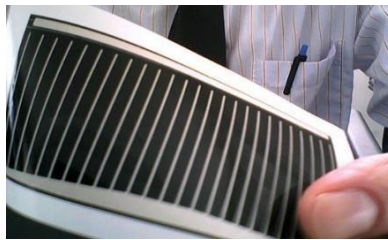


Fig 1.5: Copper indium gallium

b) **Copper zinc tin sulphide (CZTS):**

By replacing the selenium with sulphur, rare metal indium with Zinc, tin in the CIS ternary compound. CZTS is the I₂-II-IV-VI₄ quaternary compound semiconductor. They are remarkably low in toxicity. In 1988, it was made clear that the optical band gap energy was close to the ideal value of 1.45 eV as a layer for solar cell absorbers using the CZTS thin film using the atomic beam sputtering process. It has been reported that CZTS can be produced via ball milling and thin film deposition using thermal evaporation. Screen printing was used to create CZTS layers on flexible polyimide substrates after wet ball milling and sintering were used to prepare the surfaces. Using ball-milled kesterite powders, conversion efficiencies of 5.2 and 6.9% for CZTS a, respectively, have been reported (Rajeshmon et al., 2011).

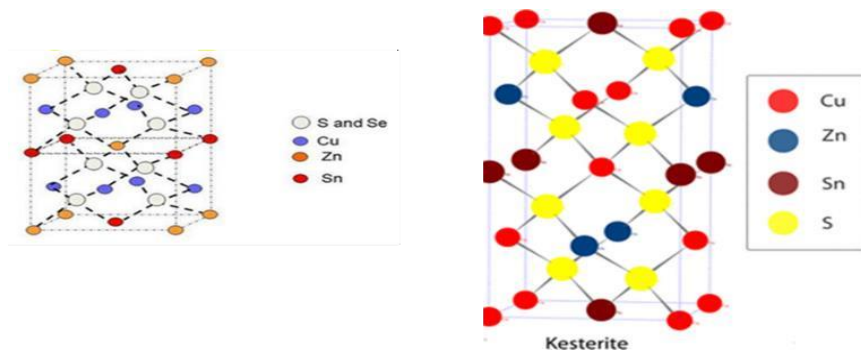


Fig 1.6: stannite & Kesterite

CZTS has a high absorption coefficient and an optimum band gap of 1.5 eV, making it a superior p-type absorber. Molybdenum (Mo) serves as the back contact in a typical CZTS hetero-junction solar cell, which also includes a p-type absorber layer of CZTS and an n-type window layer of CdS. To stop any shunting channels through the n-type layer, intrinsic zinc oxide (i-ZnO), a highly resistive material, is sandwiched between the window layer and the transparent conducting oxide (TCO) layer.

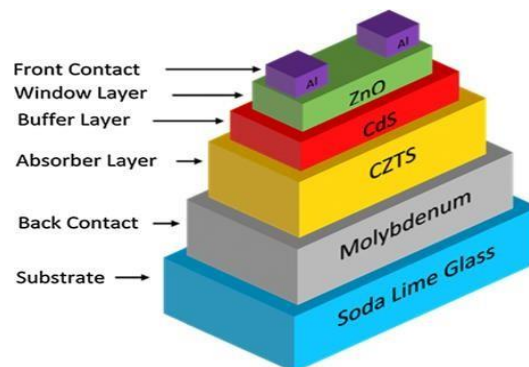


Fig 1.7: CZTS thin-film solar cell

c) Cadmium telluride (CdTe):

The second most popular photovoltaic (PV) technology is CdTe solar cells. The production of CdTe thin-film solar cells is quick and affordable, offering an alternative to traditional silicon-based technology. First Solar has achieved an experimental CdTe solar cell efficiency record of 22.1%. Moreover, First Solar stated that the typical commercial module efficiency was around 18%. With a bandgap energy that can be adjusted between 1.4 and 1.5 (eV).

cadmium telluride has the direct-bandgap material that is almost perfect for turning sunlight into electrical energy using a single connection. High throughput manufacturing techniques are used in cadmium telluride photovoltaic cell to quickly turn raw ingredients into finished modules(Lokhande et al., 2016).

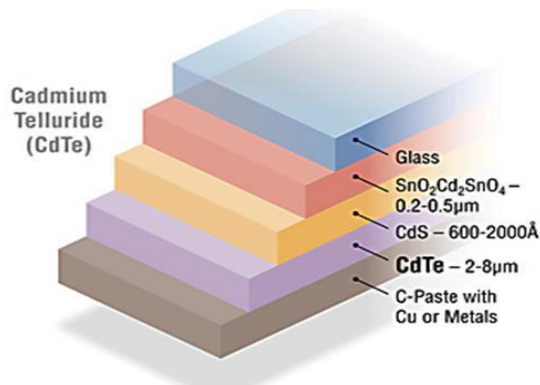


Fig 1.8: Structure of cadmium telluride solar cell

d) Copper indium selenium (CIS):

A thin sheet of CuInSe₂ on a base of clear glass or malleable metal is used to create CIS cells. The copper indium gallium di-selenide (CIGS) cell is another popular variant of this one. CIS solar cells are as durable as solar cells made of silicon and have an efficiency of up to 14%. These may cost less than Si cells since they use a thin film technology. These cells have a shortcircuit power of 95 mA and an open-circuit current of 5 V DC. The maximum power is 64 mW at 3.9V.

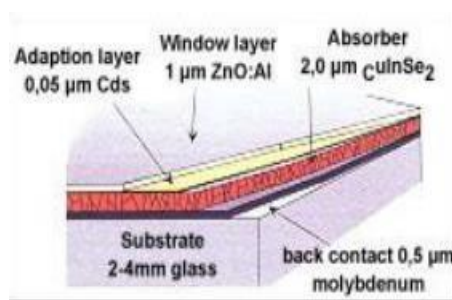


Fig 1.9: CIS solar cell

CuInSe₂-based solar cells offer the highest conversion efficiency of any thin film solar cells, exceeding 19%, and have demonstrated long-term stability. There are numerous

ways to make CuInSe_2 and other Cu chalcopyrite, from low-temperature liquid phase techniques like electrodeposition to physical vapour deposition techniques like evaporation and sputtering.

Chalcogens:

The periodic table's group 16 contains the chemical elements known as chalcogens. The oxygen family is another name for this family. Group 16 includes the elements polonium (Po), livermorium (Lv) as well as the other like elements selenium (Se), tellurium (Te), sulphur (S), and oxygen (O). With six valence electrons in total, the chalcogens all fall short of having a complete outer shell by two electrons.

They exist most frequent oxidation states 2, +2, +4, and +6. Moving down a group, it results in a decrease in electronegativity for a variety of reasons, along with an increase in atomic radius. A well-known class of inorganic glassy materials called chalcogenides contains one or more chalcogen elements. Despite the fact that chalcogens begin with oxygen, the principal chalcogenides are sulphides, selenides, tellurides, as well as polonides.

We can categorise chalcogen ions into 4 different groups based on their abundance:

- a) Mono Chalcogenides: The compound is classified as mono chalcogenide if there is only one chalcogen ion present.
- b) Di Chalcogenides: A chemical is a dichalcogenide if it contains two Chalcogen ions.
- c) Tri chalcogenides: If a compound contains three Chalcogen ions, it is a tri chalcogenide.
- d) Tetra chalcogenides: A chemical is a tetra chalcogenide if it contains four chalcogenions.

We can categorise Chalcogens into 3 groups based on their number:

- a) Binary Chalcogenides: A binary compound that contains a chalcogen.
- b) Ternary Chalcogenides: Ternary chalcogenides are ternary compounds that contain chalcogens. Nickel Ternary Chalcogenides are ternary chalcogenides that typically contain nickel.
- c) Quaternary chalcogenides: Chalcogens are present in quaternary compounds known as quaternary chalcogenides.

1.4.3. Third generation solar cell:

The goals of these photovoltaic cells are having high efficiency and cheap in cost. In these solar cells, novel techniques involving semiconductor nanoparticles were applied. The Shockley- Queisser efficiency limit, which refers to the thermodynamic energy conversion restriction of solar cells, ranges from 31% to 41%, and it is anticipated that employing semiconductor nanoparticles will allow for the circumvention of this restriction. PVCs need to perform exceptionally effectively in both optics and electronics in order to meet the demands of practical applications.

To increase optical absorption, ruthenium complex dye and semiconductor quantum dots (QDs) are used in the first two examples to expose a mesoporous Titania (TiO_2) layer. In DSSCs, the high efficiency reached thus far has reached around 14%, while in QDSSCs, it has reached about 8–10%.

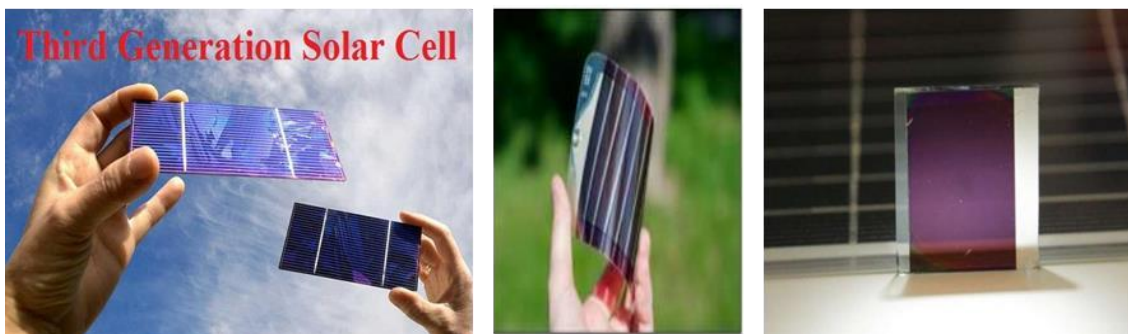


Fig1.10: Third generation solar cell

The categories of third-generation solar cells include

- Dye-sensitized solar cells
- Nanocrystal based solar cells
- Perovskite solar cells

a) Dye-sensitized solar cell:

It was created in 1991 by Dr. Brian O' Regan and Professor Michael Graetzel, and got its name because it simulates photosynthesis by absorbing light from the environment. A particular type of inexpensive photovoltaic (solar cells) cell that

effectively transforms clear light into electrical energy is called a dye-sensitized solar cell, or DSSC. Because to their material and straightforward structure, DSSCs offer a possible answer to upcoming energy issues.

These cells are comprised of mesoporous oxide electrodes covered with titanium dioxide nanoparticles. A light-sensitive dye that absorbs energy from the sun's rays is applied to this layer. Titanium dioxide is used to make solar cells because it resists electron transport better compared to any other substance. The molecular sensitizers of the dye molecule can overcome this constraint even though they can only absorb a certain number of photons from the sun. To increase their ability to capture additional photons from the sun, such solar cells are positioned on top of a semiconductor. The titanium dioxide is then positioned over a platinum-based catalyst and submerged in an electrolyte solution.



Fig 1.11: Dye-sensitized solar cell

b) Nanocrystal based cell:

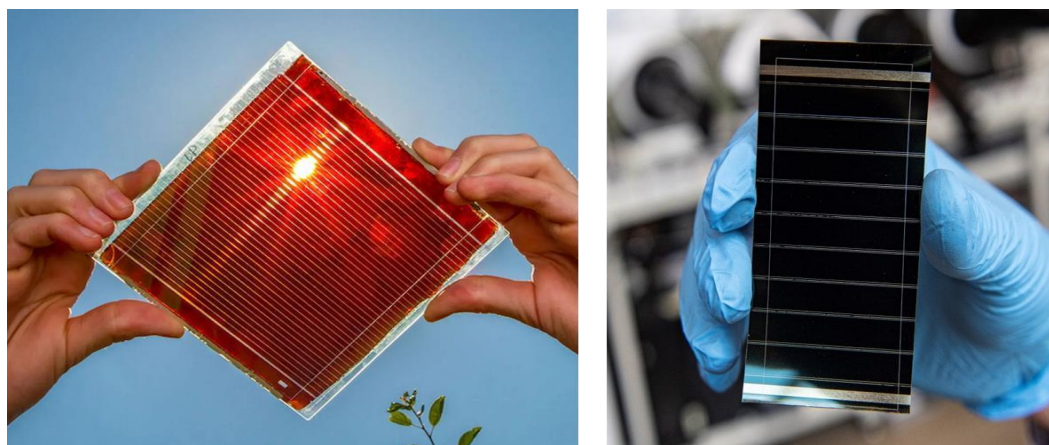
Solar cells made of nanocrystals on a substrate are known as nanocrystal solar cells. The substrates are normally silicon or different organic conductors, while the nanocrystals are commonly based on silicon, CdTe, or CIGS. Earlier fabrication techniques required costly molecular beam epitaxy procedures, while colloidal synthesis enables less expensive production. The "spin-coating" method produces a thin film of nanocrystals. In order to do this, a little quantity of the quantum dot solution must be applied on a flat substrate before being quickly rotated. The substrate is rotated until the desired thickness is reached after the fluid has evenly

diffused throughout.

It was discovered in 1991 that quantum dot-based solar cell focused on dye-sensitized colloidal TiO₂ sheets demonstrated positive efficiency of changing incident light into electrical current, which was very exciting because of the inexpensiveness of materials utilised. Future nanocrystal photovoltaic systems may have benefits like flexibility (quantum dot-polymer composite photovoltaics), cheaper prices, clean energy production, and a 65% efficiency compared to 20 to 25% for first-generation, crystalline silicon-based solar energy.

c) **Perovskite solar cells:**

A perovskite solar cell (PSC) is a form of solar cell that uses a perovskite-structured compound as that of the light-harvesting active layer, most frequently a hybrid organic-inorganic lead as well as tin halide-based material. All-inorganic caesium



lead halide and methylammonium lead halides are two examples of perovskite materials that are easy to make and inexpensive to generate. They have the capacity to produce thin, light, flexible, high efficiency, low-cost solar module

Fig 1.12: perovskite solar cells

Perovskite solar cells have been used to power low-power wireless electronics prototypes for Internet of things applications that are ambiantly powered. Many optoelectrical characteristics of perovskite cells also make them useful for solar cell applications.

1.5. Deposition methods:

➤ Physical:

- a) Thermal / electron beam evaporation
- b) DC/RF magnetron sputtering
- c) Pulsed laser deposition
- d) Molecular beam epitaxy
- e) Electric arc deposition

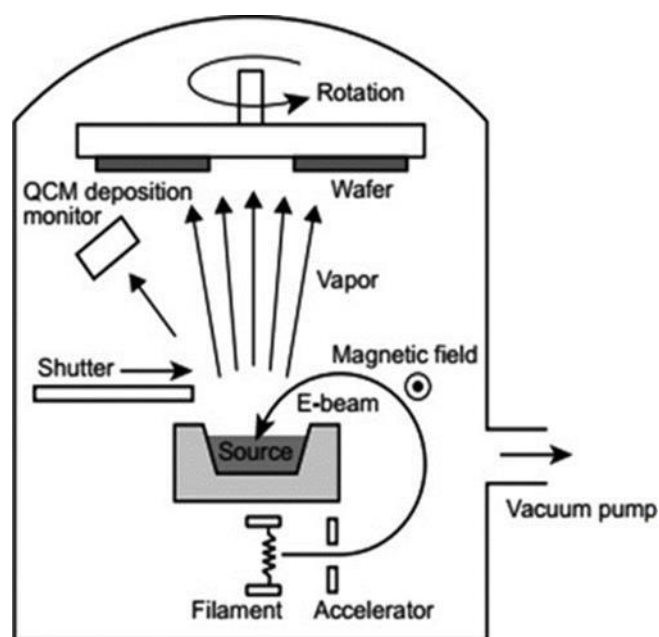
➤ Chemical:

- a) Chemical/ electro photochemical bath
- b) Hydrothermal / solvothermal
- c) Chemical vapour deposition
- d) Sol-gel
- e) Spin coating/ spray pyrolysis

1.5.1. Physical methods:

a) Thermal/ electron beam evaporation:

Electron beam evaporation, also known as E-beam or electron beam bombardment, is a type of physical vapour deposition where the target material is used as a coating which is exposed to an electron beam from one charged



tungsten filament in order to evaporate and transform it into a gaseous state for deposition here on coating material. Higher deposition speeds from 0.1 nm per minute to 100 nm per minute are possible with electron beam evaporation, leading to greater density film coatings with improved substrate adherence. There is less crucible contamination because the E-Beam system just heats the target source material and not the entire crucible.

Fig1.13: Electron beam evaporation

b) Sputtering:

The technique used to produce thin films of target material upon a substrate is called sputtering. Gas atoms, ions, and molecules are sputtered from the target surface during this procedure by injecting gaseous ions into another source material. These released particles have a certain amount of kinetic energy, which enables metal ions to move more easily over surfaces. There are two operating modes for sputtering: DC (diode and triode) and AC (radio frequency), which likewise have two configurations the magnetrons DC (balanced & unbalanced) and AC (balanced & unbalanced).

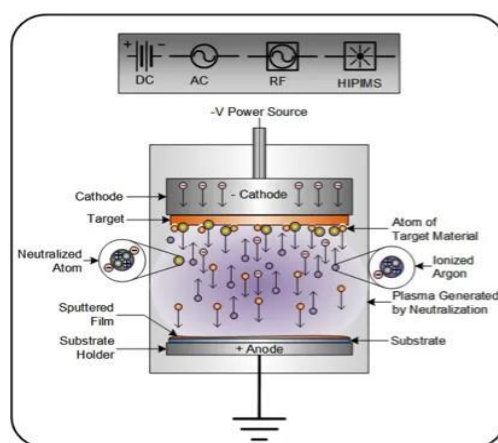


Fig 1.14: Thin film deposition by sputtering technique

a) DC sputtering:

Ionized gas molecules are used in the thin film deposition technique known as direct current (DC) sputtering to vaporise (or "sputter") molecules off the target material into plasma. Because to its low cost and great level of control, DC sputtering is the favoured approach for electrically conductive target materials. Target material is parallel to the target substrate in a vacuum chamber during the DC magnetron sputtering process. A high-quality inert gas, such as argon, is present in the vacuum chamber and becomes charged when subjected to a pulsed DC current. The gas which is present in the vacuum chamber gets ionized. As an outcome, positive ions are generated, which collect on the target face's surface and charge it positively. The release of sputtering atoms can be stopped by this gradual development of a positive charge in the dielectric.

b) RF sputtering:

Radio frequency, or RF in the process of sputtering, the electrical potential of the current is alternated at radio frequencies in a vacuum environment in order to prevent a charge from accumulating on specific target materials. RF Sputtering ionises an inert gas in a sealed chamber by passing an energy wave through it. The high energy ions strike the metal target or cathode which serves as the thin film coating, sputtering off atoms in a fine spray that covers the substrate to be coated. RF Faster deposition rates are made possible by magnetron sputtering, which uses magnets behind negatively charged cathode to hold electron over the negative charges target material and prevent them from bombarding the substrate. Because RF sputtering deposition rates generally slower and power costs are substantially greater than those of DC sputtering, RF sputtering is often employed to coat smaller substrates (Katagiri et al., 2009).

c) Pulsed laser deposition:

The thin-film coating system is physically deposited using pulsed-laser

deposition (PLD). This procedure can take place in an extremely low vacuum or with the addition of a gas mixture, like oxygen, which is frequently employed thoroughly to oxygenate the films that are being produced while oxides are being deposited. PLD's intricate workings include the laser-induced ablation of the target material, the creation of a plasma plume including highly energetic ions, electrons, and neutrals, as well as the crystallisation of the film on the heated substrate. PLD can often be broken down into four phases. Each of these stages is essential for the final film's crystallinity, homogeneity, and stoichiometry. The four stages are classified into:

- ❖ Laser absorption on the target surface and laser ablation of the target material and creation of a plasma
- ❖ Dynamic of the plasma
- ❖ Deposition of the ablation material on the substrate
- ❖ Nucleation and growth of the film on the substrate surface

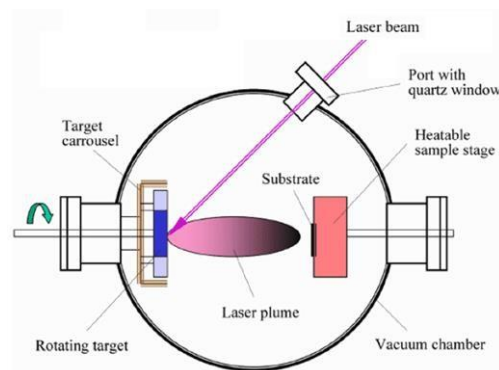


Fig 1.15: Pulsed laser deposition

Laser-target interaction:

The laser beam is fully absorbed on the target material during the initial stage. All components in the target surface are abruptly heated to about their evaporation temperature when high energy density as well as short pulse duration are used. At this temperature, the elements are exfoliated, thermally and electronically excited and collisionally separated from the target, instantly ablating them out using the identical stoichiometry as the target.

Plasma plume formation:

In accordance with the dynamic laws of gases, in the stage 2, the ablated materials do have propensity to flow in the direction of the substrate and exhibit the forward peaking phenomena, producing a plasma plume.

Deposition on the substrate:

At the third step, the high-energy species in the plasma plume impinge on the substrate surface. Some of the atoms that have been deposited on the substrate surface are sputtered by these energetic species, and a zone is created where the incoming flow and the sputtered atoms interact. Just adjacent towards this collision or thermalized zone, film growth takes place. The energetic particles condense here in order to be placed on the substrate.

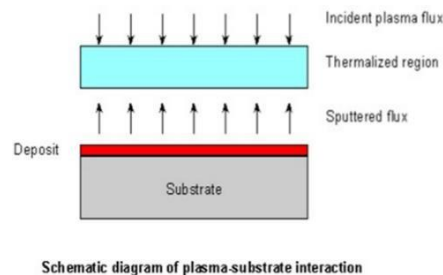


Fig1.16: Plasma substrate interaction

Nucleation and growth:

The density, energy, level of ionisation, kind of condensing material, temperature, and substrate characteristics are just a few of the variables that affect the fourth stage, nucleation, and formation of crystalline thin films. The interfacial energies between both the substrate, condensing material, and vapour have an impact on the nucleation process. The essential size of the nucleus is significantly influenced by the substrate temperature and the rate of deposition. On substrates, large nuclei produce discrete islands of film that coalesce and grow.

The surface mobility of a coated atoms, that diffuse upon that surface before locking onto a stable situation, strongly depends on the substrate's temperature, controls the formation of the crystalline film. High temperatures can lead to defect-free crystal

formation, while deposit on such a low temperature substrate can produce a poor or even amorphous crystalline structure.

d) Molecular beam epitaxy:

When thermal beams of atoms or molecules react on a clean surface of the single-crystalline substrate while being held at high temperatures and in ultrahigh vacuum, they create an epitaxial film, which is known as molecular beam epitaxy (MBE). A physical technique for thin film deposition is the MBE process. Several kinds of organic semiconductors are deposited using Molecular-beam epitaxy (MBE). In this instance, molecules are evaporated then deposited in to wafer rather than atoms. Additional versions include chemical vapour deposition-like gas-source MBE(Ranjan et al., 2021).

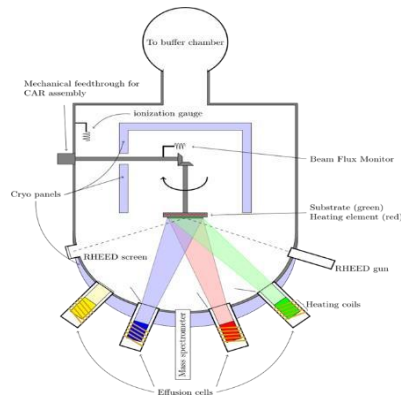


Fig 1.17: Molecular beam epitaxy

Two or more Knudsen effusion cells (K-cells), positioned at the bottom of a UHV chamber and oriented towards the middle of the chamber in which a sample holder with a substrate is, makeup the standard MBE experimental setup. Heating the K-cells to a rough temperature promotes the growth of the MBE process.

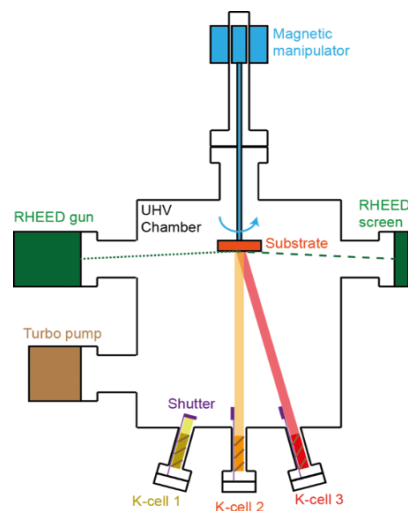


Fig 1.18: Schematic diagram of MBE

The temperature & surface atomic structure of a substrate, as well as the flux ratios of various components reaching the substrate, will all affect the final composition as well as stoichiometry of the film.

e) Electric arc deposition:

Cathodic arc deposition, commonly known as arc deposition, employs an electrical

arc to cause the cathode to emit blast ions. A vapor deposition process called cathodic arc deposition, often known as arc-PVD, uses an electric arc to evaporate material from the cathode target.

The high deposition energy of the condensing atoms, that is necessary for film growth to support adhesion and to obstruct columnar growth, is what draws people to the CAD method. These energies depend on the substance and for carbon and iron, respectively, vary from 25 to 55 eV. Ion-surface interaction theory-based calculations of the energies needed

for high-quality film formation further suggest that energies of the range of 25–100 eV are also preferable for triggering surface atom displacements while retaining crystalline nature of the underlying bulk layers. The creation of macroparticles (MPs), with sizes ranging from 0.1 to 10 microns in growing films, is a drawback of the CAD process.

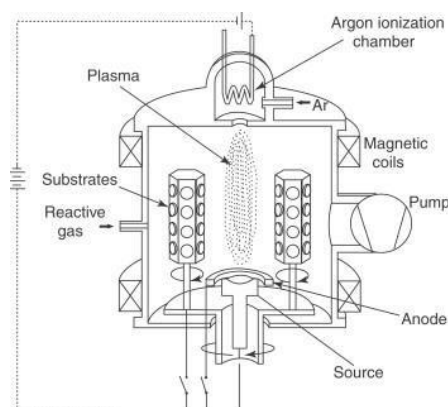


Fig 1.19: Arc deposition method

1.5.2. Chemical method:

a) Chemical bath deposition:

A controlled precipitation of such a substance from the solution onto a suitable substrate is the goal of the Chemical Bath Deposition process. The very first CBD thin films were created in 1884, and for a very long time, this technique was only applicable to PbS and PbSe. This technique has been used to generate a variety

of chalcogenide and chalcopyrite materials just after deposition of CdS. Besides from glass, a variety of substrates like ebonite, iron, steel, porcelain, and brass were used in CBD. The films were even, adhesive, and strong enough to resist a lot of rubbing.

By adjusting the deposition parameters, such as temperature, precursor concentration, the use of complexing agents, and solution pH, it is feasible to regulate the layer thickness and chemical composition in this method.

This technique relies on the formation of thin films from aqueous solutions, either through the passage of a current or through chemical reactions under the right circumstances. These films are typically not of high purity due to the nature of their preparation processes. The precise composition of thin films can be attained with the proper control of the deposition conditions. The most alluring benefit of this approach is its capacity to coat big areas in a repeatable and affordable process.

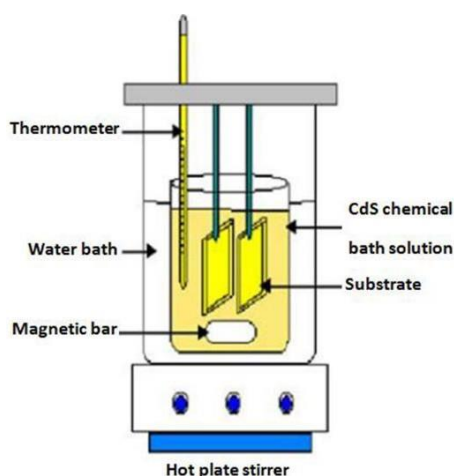


Fig 1.20: Schematic diagram of chemical bath deposition

b) Hydrothermal / solvothermal:

A solvothermal process is one that occurs in a sealed reaction vessel that

causes the decomposition or chemical reaction of one or more precursors while the solvent is present, at a temperature greater than the solvent's boiling point. The pressure may be natural or artificial.

The solvothermal system may be heterogeneous or homogeneous, and it may be undersubcritical or supercritical conditions, depending on the experimental parameters (pressure and temperature). The first applications of hydrothermal processes were in the geosciences for the synthesis of minerals, in materials science for the crystallisation of useful materials, and in hydrometallurgy for the creation of novel techniques for leaching ores.

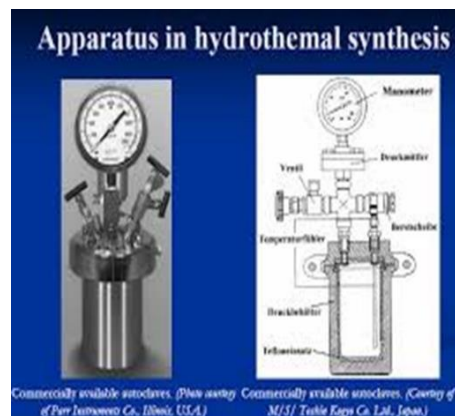


Fig 1.21: schematic diagram of solvothermal/hydrothermal

c) **Chemical vapour deposition:**

Chemical vapor deposition (CVD) is a commonly used technique for depositing thin films in thin-film solar cells. CVD involves the reaction of precursor gases in a high-

temperature environment to form a solid thin film on a substrate. The resulting thin film can have excellent uniformity, high purity, and can be deposited at high growth rates.

CVD can offer several advantages over other deposition techniques, including the ability to deposit high-quality thin films on large substrates, the ability to deposit thin films with precise thickness control, and the ability to deposit thin films at relatively high growth rates. CVD involves the deposition of a thin film of a material onto a substrate using chemical reactions in the gas phase. However, CVD can also be expensive and requires specialized equipment and expertise to implement.

In thin-film solar cells, CVD is used to deposit the semiconductor material onto a substrate, which serves as the base for the solar cell. The semiconductor material used is typically a group III-V compound, such as gallium arsenide (GaAs), or a group II-VI compound, such as cadmium telluride (CdTe).

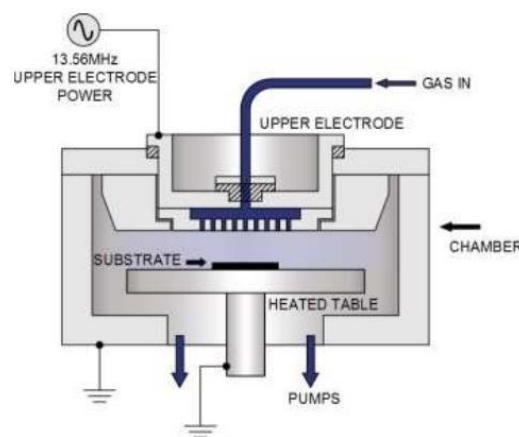


Fig 1.22: Working principle of Chemical vapour deposition

To provide a clean surface for deposition, the substrate requires cleaning and fully prepared. In a chamber, a mixture of reactant gases is introduced. A precursor gas is frequently present in the gas mixture. The substrate gets heated to encourage the chemical processes required for deposition. A thin layer of the semiconductor material is created when the reactant gases react on the heated substrate. The surplus reactant gases are expelled from the chamber while the substrate is cooled.

The advantages of CVD in thin-film solar cell production include the ability to deposit high- quality films with precise control over the thickness and composition. CVD is also a relatively low-cost technique compared to other deposition methods, such as molecular beam epitaxy (MBE).

Because CVD processes and equipment can be expensive, it is not always a solution that is economically viable for large-scale manufacturing. Thin film deposition can take a very long period with CVD, which reduces production and raises expenses. It might be difficult to

expand the deposition chamber or the substrate area in CVD without compromising the consistency and quality of the produced thin films.

The chemical vapour deposition is classified according to their operating condition.

They are

- Atmospheric pressure CVD
- Low pressure CVD
- Ultra-high vacuum CVD
- Sub atmospheric CVD
- Plasma enhanced CVD

Atmospheric pressure CVD:

Doped and undoped oxides are deposited using the APCVD process, which is a CVD technique at atmospheric pressure (normal pressure). Due to the comparatively low temperature, the deposited oxide has a low density and a modest coverage. New tools enable the APCVD to experience a Renaissance. The high wafer throughput of this method is a significant benefit.

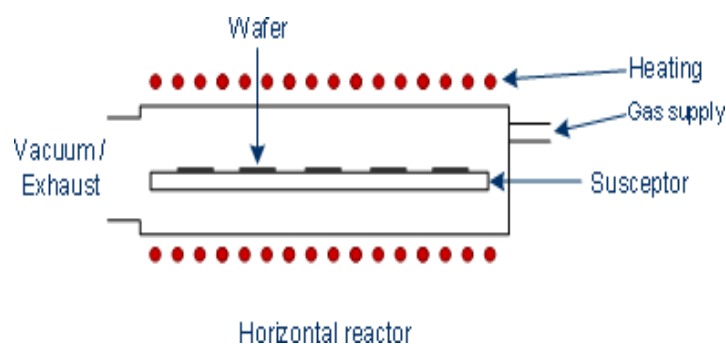


Fig 1.23: Illustration of horizontal Atmospheric CVD reactor

Low pressure CVD:

A hoover is used in LPCVD. With LPCVD techniques, a high conformity of almost 1 is possible. This is due to the atmospheric pressure, which is 10 to 100 Pa, which causes the particles to flow in an uneven manner. Due to collisions, the particles disperse and cover both horizontal and vertical surfaces. An extremely high temperature of up to 900 °C supports the compliance. The density and stability are relatively high when compared to APCVD (Bankar et al., 2021).

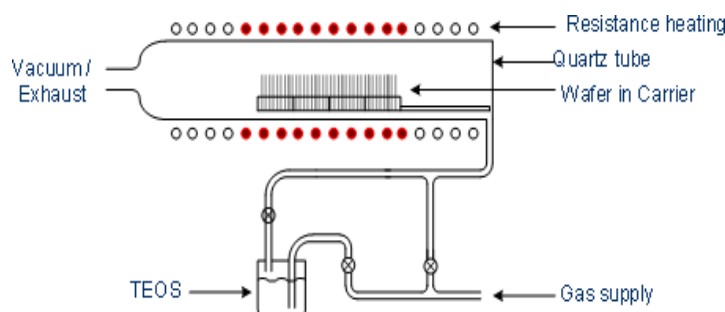


Fig 1.24: Illustration of Low- pressure CVD reactor

Ultra-high vacuum CVD:

For the creation of high-quality thin films, an ultra-high vacuum (of the order of 10^{-6} torr) is a crucial need. The production of many electrical and optical devices requires the use of high-quality thin films. To produce the necessary quantity of vacuum, there are many pumps on the market. These pumps are often divided into two categories: high vacuum pumps and forward vacuum pumps. Rotary pumps are an example of forward vacuum pumps, whereas turbo molecular pumps and diffusion pumps are examples of high vacuum pumps.

Sub atmospheric CVD:

On structures with high aspect ratios, sub-atmospheric CVD (SACVD) has demonstrated good film characteristics and planarization capabilities. The SACVD reactor has the ability to operate in plasma mode and at pressures as low as almost atmosphere.

Plasma enhanced CVD:

In the process known as plasma-enhanced chemical vapour deposition (PECVD), thin films of different materials are deposited at a lower temperature than in conventional CVD. Due to its capacity to coat surfaces that wouldn't be capable of enduring the temperatures of more conventional CVD processes, plasma enhanced chemical vapour deposition (PECVD), a low temperature vacuum thin film deposition process, has a very strong position in the semiconductor industry.

There are three fundamental requirements for the PECVD process

- (a) the production of plasma through ionisation of atoms and molecules
- (b) a pressure management system to sustain the plasma state and
- (c) a reaction chamber.

By heating the gas or using electrical energy, plasma can be created, which is a fully or partially ionised gas or a mixture of charged particles, neutral atoms, and electrons. As a result, although being rich in energy, the plasma state is neutral. When high vapour pressure precursors are injected into the PECVD chamber, the precursor becomes dissociated and activated as plasma, enabling the film to be deposited at a temperature that is lower. This approach has the advantages of high deposition rate, low temperature, and the ability to use inorganic as well as organic substances as precursors.

Lower deposition temperatures, good conformance and step coverage on uneven surfaces, better control of the thin film process, and high deposition rates are the main advantages of PECVD over traditional CVD.

PECVD temperatures range from ambient temperature to 350°C, whereas regular CVD temperatures are typically done in the 600°C to 800°C range. This permits effective applications in situations where the higher CVD temperatures could potentially harm the device or substrate being coated. It reduces tension

between thin film layers with varying thermal expansion/contraction coefficients by working at a lower temperature. This enables extremely high levels of electrical bonding and performance.

Due to the fact that CVD is a diffusive gas-driven process, it offers superior coverage on uneven surfaces like walls or trenches that have a high degree of conformance. As a line-of-sight deposition, PVD coatings, on the other hand, can provide significant variation in thin film depth if imperfections obscure areas from coating. Since the plasma stream may completely encircle the substrate during PECVD, the line-of-site problem for highly conformal thin films is greatly diminished.

Excellent control of material qualities, such as density and hardness, purity, roughness, or the refractive index of optical films, can be achieved by adjusting the plasma's parameters. PECVD produces some of the highest film quality at some of the quickest deposition rates.

Unique compounds and films can be generated with PECVD, which is also able to make films with exceptionally high solvent and corrosion resistance as well as chemical and thermal stability.

d) Sol-gel:

Sol-gel is a method for producing thin films of materials that involves the transformation of a solution into a solid network through chemical reactions. CZTS, or copper zinc tin sulfide, is a promising material for use in thin-film solar cells due to its abundance, low toxicity, and suitable optoelectronic properties. Sol-gel techniques can be used to deposit CZTS thin films on a variety of substrates, including glass, metal, and polymer films. The sol-gel process involves the mixing of metal precursors and sulfur-containing compounds in a solvent to form a sol, which is

a stable colloidal suspension of nanoparticles. The sol is then deposited onto a substrate and allowed to dry, forming a thin film.

The resulting CZTS thin films can be further annealed to improve their crystallinity and electrical properties. The sol-gel method offers several advantages over other techniques for producing CZTS thin films, including low processing temperatures, low cost, and scalability.

However, the efficiency of CZTS solar cells remains relatively low compared to other types of solar cells. Research efforts are focused on improving the material quality and device design to enhance the conversion efficiency of CZTS thin-film solar cells (Agawane et al., 2015).

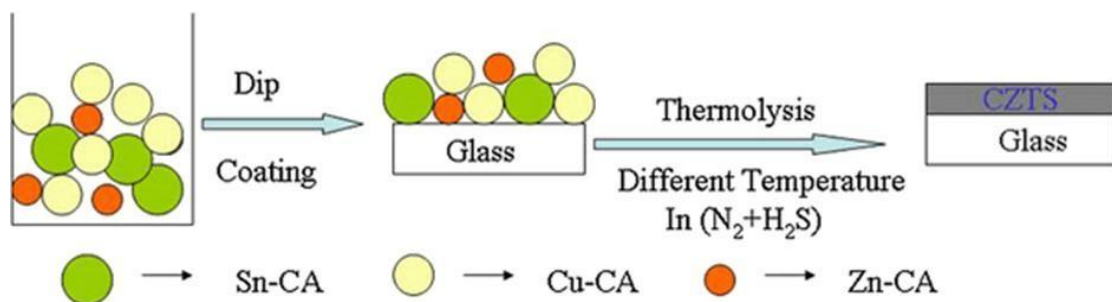


Fig 1.26: Sol-gel technique

e) Spin coating/ spray pyrolysis

Spray pyrolysis is a procedure in which a solution is sprayed on a heated surface, where the ingredients react to produce a chemical compound, resulting in the deposition of a thin film. The chemical reactants are chosen so that, at the deposition temperature, the products other than the intended molecule are volatile.

A method for depositing thin layers of materials onto a substrate is spray

pyrolysis. Spray pyrolysis can be employed to deposit the CZTS layer onto a substrate like glass or a flexible plastic material in the context of CZTS (copper zinc tin sulphide) thin filmsolar cells(Orava et al., 2013).

A precursor solution containing the required metal ions and sulphur is atomized into minute droplets using a nozzle during the spray pyrolysis procedure. After being sprayed onto the heated substrate, these droplets react and create a thin layer of CZTS. To guarantee that the resultant film has the correct composition and structure, the substrate temperature and other process variables are carefully regulated.

Comparatively speaking to other deposition techniques like sputtering or chemical vapour deposition, spray pyrolysis is a rather straightforward and affordable process. It is suitable with many different kinds of substrates, including flexible substrates, and may also be utilised to deposit large-area films.

However, the calibre of the film produced by spray pyrolysis can have an impact on the performance of CZTS thin film solar cells. The composition, thickness, and crystal structure of the film, among other factors, can have a significant impact on the solar cell's stability and performance. Therefore, to produce high-quality CZTS thin films for solar cell applications, the spray pyrolysis process needs to be carefully optimised.

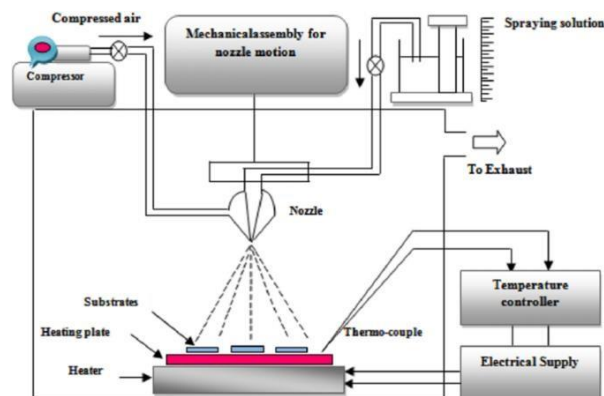


Fig 1.27: schematic diagram of Spray pyrolysis

CHAPTER 2

LITERATURE SURVEY

2.1 Title: Fabrication of 3.01% power conversion efficient high-quality CZTS thin film solar cells by a green and simple sol–gel technique

Author: G.L. Agawane, A.S. Kamble, Jin Hyeok Kim

Publication: Material letters

Year: 2015

Fine quality $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin films were prepared by a non-toxic, simple and economical sol–gel and spin-coating technique. The CZTS thin films were prepared on Molybdenum coated soda lime glass substrates. The films were annealed at three different temperatures viz. 525, 550 and 575 $^{\circ}\text{C}$ under H_2S gas atmosphere to study the effect of annealing temperature on the morphological, structural, chemical, compositional, optical and photovoltaic properties of the CZTS thin films. The X-ray diffraction and Raman spectroscopy investigations on the CZTS thin films showed formation of the pure kesterite structure.

The X-ray fluorescence studies demonstrated that all the CZTS thin films were nearly stoichiometric having Zn rich composition. All the annealed films were further subjected to fabrication of solar cells as an SLG/Mo/CZTS/CdS/i-ZnO/AZO/Al grid. The best solar cell showed a short-circuit current density of 14.57 mA/cm^2 , open-circuit voltage of 513 mV, fill factor of 40% and power conversion efficiency of 3.01% under air mass 1.5 (100 mW/cm^2) illumination.

2.2 Title: Current challenges and future prospects for a highly efficient (> 20%) kesterite CZTS solar cell

Author: Krishan Pal, Pawan Singh, Abhishikta Bhaduri, Khem B. Thapa

Publication: Solar energy materials and solar cell

Year:2019

CZTS has kesterite structure and the composition's formula is $\text{Cu}_2\text{ZnSn}(\text{S}/\text{Se})_4$. The efficiency of CZTS-Se (Copper Zinc Tin-Sulphur-Selenium) solar cell, ~12.6%, is much lower than the efficiency of CIGS (Copper Indium Gallium Selenium) solar cell, ~22.6%. But the CZTS-Se may be the counterpart of the CIGS and the efficiency may be increased up to 32.2% as theoretically predicted by the Shockley-Queisser (SQ) limit. In solar cell technology, it has been depicted that the efficiency of the solar are affected by the two parameters:

- a) variation of the solar insolation and
- b) quality of the materials.

Besides this, the narrow phase stability of quaternary phases, unfavourable band alignments, mid-gap states and band tails are main reasons of deficit in the efficiency of kesterite due to the coexistence of the secondary and ternary phases, carrier recombination at the interfaces, defects and series resistances. As a result, the kesterite solar cell has the fluctuated open circuit voltage and the loss of energy. In addition to this, the champion CZTS-Se solar cell is not so environmentally friendly because Se is the toxic and the rare earth element. This review provides the vital approaches by discussing the proper materials processing and the appropriate solution to enhance the efficiency of kesterite (CZTS, CZTSe and CZTS/Se) solar cells. Due to the large area quality, high absorption and low-cost materials of the kesterite, it may be used directly in harvesting the solar energy. We have also discussed how to reduce the recombination of the electron-hole pairs by using the interfacial layer so that the efficiency of the kesterite solar cells can be improved (Li et al., 2018).

2.3 Title: Characterization of a CZTS thin film solar cell grown by sputtering method

Author: Tara P. Dhakal, Chien–Yi Peng, Charles R. Westgate

Publication: Solar energy

Year: 2013

We report the performance of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) thin film solar cell that showed

efficiency in the range of 6.2% without an anti-reflection coating. Initially, the CZTS precursor film was co-sputtered using three different targets; copper (Cu), tin sulfide (SnS) and zinc sulfide (ZnS). The Cu target was subjected to DC power, and RF power was used for the SnS and ZnS targets. The as-grown CZTS film was sulfurized in a H₂S/N₂ environment at 525 °C, which re-crystallized the film with grain sizes in the range of 1 μm. Cadmium sulfide (CdS) was used as the n-type layer. Current–voltage (I–V), quantum efficiency (QE) and capacitance–voltage (C–V) measurements were used to characterize the cell device. The modelling and analysis of QE and CV data showed that a significant portion of the CZTS layer did not contribute to the photo-generation. Optimizing CZTS phase purity, improving QE in the broader wavelength region, and increasing minority carrier lifetime are necessary steps to further improve CZTS device performance.

2.4 Title: Preparation of Cu₂ZnSnS₄ (CZTS) Sputtering Target and Its application to the Fabrication of CZTS Thin-film Solar Cells.

Author: Yu-Pin Lin, Yen-Chih Chen, Kun-Ping

Huang. **Publications:** Journal of Alloys and Compounds **Year:** 2016

The CuS, ZnS and SnS₂ raw powders were adopted as the starting materials for preparing the 2-inch Cu₂ZnSnS₄ (CZTS) sputtering target. The powders were mixed at various molar ratios

of Cu:Zn:Sn:S = 1.6:1:1:4, 1.8:1:1:4 and 2:1:1:4, pressed into 6-mm pellet forms, and then sintered at different temperatures for 8 hrs. Accordingly, the influence of powder constitution and heat-treatment conditions on the microstructure, composition and morphology of CZTS pellets were investigated.

Microstructure and composition analyses indicated that the sample prepared with the Cu molar ratio of 1.6 and sintered at 600 °C for 8 hrs forms the kesterite CZTS single-phase structure with the Cu-poor/Zn-rich composition. The 2-inch CZTS sputtering target was prepared by utilizing the method established by the study of 6-mm pellets and adopted for depositing the CZTS thin films. The CZTS layer deposited at the working pressure of 1 m torr followed by the sulfurization at 570 °C for 1 hr possessed

the stoichiometry of $\text{Cu}_{24.15}\text{Zn}_{14.73}\text{Sn}_{10.75}\text{S}_{50.37}$ which is the closest to the ideal stoichiometric ratio of 2:1:1:4. Moreover, it exhibited the bandgap of 1.5 eV, p-type carrier concentration of $2.8 \times 10^{17} \text{ cm}^{-3}$ and mobility of $8.61 \text{ cm}^2 \cdot \text{V}^{-1} \text{ sec}^{-1}$

Such a CZTS layer was implanted in the thin-film solar cells with the device structure of Mo/CZTS/CdS/i-ZnO/IZO/Al. Under the AM1.5 illumination condition, the CZTS thin-film solar cell sample with the open-circuit voltage of 0.52 V, the short-circuit current density of 19.17 mA/cm^2 , the fill factor of 52.7% and the conversion efficiency of 5.2% was achieved.

2.5 Title: Mechano-synthesis, deposition and characterization of CZTS and CZTSe materials for solar cell applications

Author: T.S. Shyju, S. Anandhi, P.

Kuppusami **Publication:** Journal of solid-state chemistry **Year:** 2015

Mechano-synthesis of nanocrystalline powders of CZTS and CZTSe by ball milling technique and the physical properties of thermally evaporated CZTS and CZTSe thin films as a function of substrate temperature are investigated. Nanocrystalline Cu–Zn–Tin–Sulphide (CZTS) and Cu–Zn–Tin–Selenide (CZTSe) powders synthesized by ball milling at different milling time using the source materials of Cu, Zn, Sn, S (or) Se in the ratio 2:1:1:4 are investigated. The above synthesized powder was thermally evaporated on glass substrate kept at room temperature and 673 K under a vacuum of 10^{-6} mbar to prepare quaternary compound semiconducting thin films in a single step process. The synthesized powder and deposited CZTS and CZTSe thin films belong to tetragonal crystal system. Raman spectra reveal that the synthesized nanocrystals are pure without any secondary phases. A gradual reduction in optical bandgap of films was observed with increasing substrate temperature due to increased crystallinity of the films. The changes in surface morphology of the films with respect to substrate temperature were studied by scanning electron microscopy and atomic force microscopy. Electrical studies indicate that the deposited films have p-type conductivity.

2.6 Title: CZTS based thin film solar cells

Author: M P Suryawanshi, G L Agawane, J H

KimPublication: Energy materials

Year:2013

Today's thin film photovoltaic technologies comprising CuInS₂ (CIS), CuInGaSe₂ (CIGS) and CdTe rely on elements that are costly and rare in the earth's crust (e.g. In, Ga, Te) and are toxic (e.g. Cd). Hence, in future cost reduction and increased production, using abundantly available non-toxic elements, seem to be the main issues. Cu₂ZnSnS₄ (CZTS), having the kesterite structure, is one of the most promising absorber layer candidates for low-cost thin film solar cells, because of its suitable direct band gap between 1.4 and 1.5 eV and large absorption coefficient, over 10⁴ cm⁻¹. It is also composed of earth abundant and non-toxic elements, promising price reductions in future. Recently, research in this area has gained momentum due to the desirability of producing Ga, In and Cd free absorber layers and the potential to obtain new insights. Hence, a review of recent literature is urgently warranted.

The CZTS progress and present status of CZTS thin film solar cells has been reviewed, with the hope of identifying new paths for productive research.

2.7 Title: Role of precursor solution in controlling the opto-electronic properties of spraypyrolyzed Cu₂ZnSnS₄ thin films

Author: V G Rajeshmon, C Sudha Kartha, K P Vijayakumar

Publication: solar energy

Year:2011

Thin films of Cu₂ZnSnS₄, a potential candidate for application as absorber layer in thin filmsolar cells, were successfully deposited on soda lime glass substrates using spray pyrolysis and the effect of variation of precursor on the structural and opto-electronic properties was investigated. We used stannous as well as stannic chloride as precursors of tin in the spray solution. All the films exhibited kesterite structure with preferential orientation along the

(1 1 2) direction. But crystallinity and grain size were better for stannic chloride-based films. They also possessed a direct band gap of 1.5 eV and the absorption coefficient was >10⁴ cm⁻¹. Carrier concentration and mobility could be enhanced and the

resistivity reduced by two orders by using stannic chloride in spray solution. Junction trials were performed with CZTS films prepared using stannic chloride precursor as the absorber layer and indium sulfide as the buffer layer. XPS depth profiling of the junction was done. Formation of CZTS could be confirmed and also information about the junction interface could be obtained from the XPS results. We obtained an open-circuit voltage of 380 mV and short-circuit current density of 2.4 mA/cm².

2.8 Title: Chemical deposition method for metal chalcogenide thin films

Author: R S mane, C D Lokhande

Publication: Materials chemistry and physics

Year:2000

Chemical methods for creating metal chalcogenide thin films are currently receiving a lot of attention due to their relative affordability, simplicity, and suitability for large-area deposition. Since these are low temperature processes, they prevent substrate oxidation and corrosion and

can be used with a variety of substrates, including insulators, semiconductors, and metals. These are slow processes that enable crystallites to have improved grain structure and better orientation. Film growth can occur via ion-by-ion condensation of the materials on the substrates or via the adsorption of colloidal particles from the solution on the substrate, depending on the deposition circumstances. These techniques have been used to deposit thin films of the group II–VI, V–VI, III–VI, etc. Metal chalcogenide films are used in a variety of applications, including solar selective coatings, solar control, photoconductors, solid state and photoelectrochemical solar cells, optical imaging, hologram recording, optical mass memory, etc.

In the current review article, we have provided a detailed explanation of the metal chalcogenide thin film chemical bath deposition process, which can produce films of high quality. They detail their preparational characteristics, structural, optical, and electrical properties, etc. Also covered is the theoretical underpinning required for the chemical deposition of thin films.

2.9 Title: Electrical and optical properties of CZTS thin films prepared by SILAR method

Author: J Henry, K Mohanraj, G

Sivakumar **Publication:** Journal of Asian
ceramic societies **Year:** 2015

In the present work, Cu₂ZnSnS₄ (CZTS) thin film was deposited onto the glass substrate by simple and economic SILAR method and its structural, morphological, optical and electrical properties were analysed. X-ray diffraction (XRD) analysis confirms the formation of CZTS with kesterite structure and the average crystallite size is found to be 142 nm. Scanning electron microscope (SEM) image shows that the film has homogeneous, agglomerated surface without any cracks. The prepared CZTS film shows good optical absorption (10^4 cm^{-1}) in the visible region and the optical band gap energy is found to be quite close to the optimum value of about 1.54 eV for solar cell application. The refractive index of the prepared film is found to be 2.85. The electrical resistivity of the film is found to be $\sim 10^{-2} \Omega \text{ cm}$ at room temperature.

2.10 Title: Development of CZTS -based thin film solar cells

Author: Hironori Katagiri, Kazuo Jimbo, Akiko Takeuchi

Publication: Thin solid films

Year: 2009

The low cost, environmental harmless Cu₂ZnSnS₄ (CZTS)-based thin film solar cells are fabricated by using abundant materials. The CZTS film possesses promising characteristic optical properties; band-gap energy of about 1.5 eV and large absorption coefficient in the order of 10^4 cm^{-1} . All constituents of this CZTS film, which are abundant in the crust of the earth, are non-toxic. Therefore, if we can use CZTS film practically as the absorber of solar cells, we will be free from both of the resource saving problem and the environmental pollution.

In our CZTS project, CZTS absorber films were prepared by two independent techniques. One is three rf sources co-sputtering followed by annealing in sulfurized atmosphere. The latest conversion efficiency of over 6.7% was achieved by this technique. The other is co-evaporation

technique. CZTS films were grown on Si (100) by vacuum co-evaporation using elemental Cu, Sn, S and binary ZnS as sources. XRD patterns indicated that the polycrystalline growth was suppressed and the orientational growth was relatively induced in a film grown at higher temperatures.

In this presentation, the development of CZTS-based thin film solar cells will be surveyed.

CHAPTER 3

Aim:

Characterization and synthesis of CZTS (copper zinc tin sulphide) thin film solar cells aim to develop a cheap, efficient, and environmentally friendly substitute for current silicon-based solar cells. CZTS is a promising material for solar applications due to its high absorption coefficient, acceptable bandgap, and abundance of its constituent elements.

To fully exploit their potential as a solar cell material, CZTS thin films must be synthesized with high-quality ingredients and thoroughly studied to understand their structural, optical, and electrical properties.

Scope:

The characterization and synthesis of CZTS thin film solar cells covers a range of techniques to improve the synthesis of CZTS thin films, such as chemical bath deposition, spray pyrolysis, and co-evaporation. Methods including X-ray diffraction, scanning electron microscopy, transmission electron microscopy, UV-visible spectroscopy, and electrical tests can be used to determine the crystalline structure, surface morphology, optical properties, and electrical properties of the CZTS thin films.

Studying the performance of the solar cell devices, such as the open-circuit voltage, short-circuit current density, and power conversion efficiency, is also part of the characterization and synthesis of CZTS thin film solar cell.

By optimising the synthesis process and device architecture, including the incorporation of buffer layers, optimising thicknesses, and interface engineering, it is hoped to increase the performance of CZTS solar cells.

In order to produce effective and sustainable solar cell technologies, the characterisation and synthesis of CZTS thin film solar cells is a multidisciplinary field that encompasses material science, physics, chemistry, and engineering.

CHAPTER 4

MATERIALS AND METHODOLOGY

4.1 Material:

Copper Zinc Tin Sulphide

Chemical Name: Copper Zinc Tin Sulphide

Chemical Formula:

$\text{Cu}_2\text{ZnSnS}_4$ Molar Weight:

439.47

Melting Point: 990

°C Boiling Point:

N/A Density: 4.56

g/cm^3

Appearance: Dark green to black crystals or solids in various forms (pelletizing, sputtering) Solubility: Insoluble in H_2O

Crystal phase: Tetragonal

4.2 Methodology:

4.2.1 Mechanosynthesis:

Due to its availability, non-toxicity, and high absorption coefficient in the visible range, CZTS (Copper Zinc Tin Sulphide) is a potential material for thin film solar cells. Making CZTS nanoparticles using Mechanosynthesis is an easy and affordable process that can be used to create thin films for applications in solar cells.

The mechanosynthesis of CZTS is carried out using SPEX Sample Prep 8000D Dual

ball mill. The compound formation depends on many parameters such as milling speed, milling time, ball-to-powder weight ratio, milling type, particle size and material of the grinding balls. Stability of metal which runs in 80 the present work, elemental Copper (Cu), Zinc (Zn), Silicon (Si) and Selenide (Se) were mixed in the ratio of 2:1:1:4 and ball to powder ratio was kept at 2:1, and the powders were milled in a stainless steel vial with stainless steel balls at the millingspeed of 2750 rotations per minute (RPM). The experiments were performed for a different period based on the type of materials used and previous results, the period is calculated (Shyjuet al., 2015).



Fig 4.1: Ball milling

Advantages:

- i. Cost-effective: Because CZTS thin film solar cells use readily available, inexpensive raw ingredients, their production costs are quite low.
- ii. High efficiency: CZTS thin film solar cells have demonstrated an efficiency of up to 12%, positioning them as an appealing option for commercial solar cell applications.
- iii. Environmentally friendly: CZTS thin film solar cells are environmentally friendly alternatives to other types of solar cells because they are built with plentiful, non-toxic ingredients.
- iv. Flexibility: CZTS thin film solar cells can be manufactured flexible, enabling the use of these solar cells in a variety of flexible applications, such as wearable

electronics and portable gadgets.

Disadvantages:

- i. CZTS thin-film solar cells may experience stability problems as a result of the presence of sulphur in the CZTS layer. As a result, the device may eventually deteriorate and lose efficiency.
- ii. Low open-circuit voltage: CZTS thin film solar cells' overall efficiency may be constrained by their lower open-circuit voltage when compared to other solar cell types.
- iii. Restricted scalability: It is challenging to manufacture large-scale devices due to the restricted scalability of the current mechanosynthesis techniques utilised for CZTS thin film solar cell fabrication.

Applications:

- i. Photovoltaic systems that are integrated into buildings: CZTS thin film solar cells can be incorporated into building facades and rooftops, offering a renewable energy source for structures.
- ii. CZTS thin-film solar cells can be used to power portable electronics, including laptops and cell phones.
- iii. Vehicles that run on solar power: CZTS thin-film solar cells can be employed to power electric cars, reducing their dependence on fossil fuels.
- iv. Applications off-grid: CZTS thin film solar cells can be used in off-grid settings, such as in rural areas or developing nations without access to a dependable electrical grid.

- In order to examine the structure and characteristics of a variety of materials, including metals, ceramics, polymers, minerals, and biological materials, XRD is frequently employed in the domains of materials science, chemistry, geology, and other scientific disciplines. It is a non-destructive method that can give important details about a material's interior structure without endangering it (Shelke et al., 2017).
- By placing the sample in the path of the X-ray beam and measuring the intensity of the scattered X-rays at various angles, the diffraction pattern is obtained. The distance between atoms in the crystal lattice and the X-ray wavelength determine the angle at which the X-rays are dispersed.
- The number of atoms in the crystal that are in a particular orientation to scatter X-rays is correlated with the intensity of the diffracted X-rays. The resulting diffraction pattern typically consists of a number of peaks that represent the diffraction angles for various crystal planes.
- These peaks are distinguished by their location, intensity, and shape, which are connected to the material's crystal structure. The crystal structure, lattice parameters, and crystal orientation of the sample are only a few of the structural details that may be ascertained using XRD. Additionally, it can be used to examine phase transitions, impurities in the crystal lattice, and the effects of temperature, pressure, and other environmental factors on the crystal structure (Vanalakar et al., 2015).

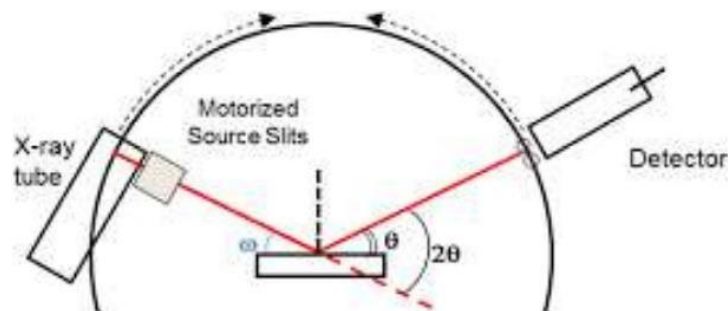


Fig5.1: The principle working of X-ray diffraction.

UV Vis Spectroscopy:

- CZTS (Copper Zinc Tin Sulphide) is a promising material for thin-film solar cells due to its high absorption coefficient and acceptable bandgap for effective solar energy conversion. UV-Vis spectroscopy is a useful method for examining the optical properties of materials (Beun et al., n.d.).
- UV-Vis spectroscopy can be used to assess the material's absorption spectra in CZTS thin-film solar cells in order to ascertain its bandgap energy and absorption coefficient. The solar cell's design can then be optimised to increase performance using this information.
- The impact of various processing parameters, such as the temperature of annealing and deposition method, on the optical characteristics of CZTS thin films can also be studied using UV-Vis spectroscopy. This can offer insightful information on the mechanism of CZTS formation and assist in streamlining the manufacturing procedure to increase solar cell efficiency.
- Generally speaking, UV-Vis spectroscopy is an effective method for analysing the optical characteristics of CZTS thin films and can offer crucial insights for the creation of high-performance thin-film solar cells.

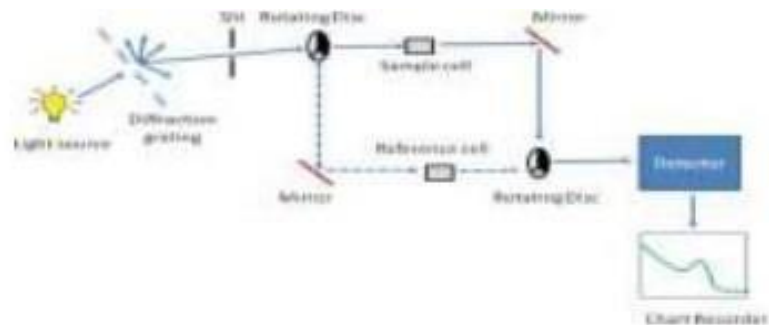


Fig5.2 : The ultra-violet visible spectroscopy

Raman spectroscopy:

Raman Spectroscopy is a non-destructive chemical analysis technique which provides detailed information about chemical structure, phase and polymorphy, crystallinity and molecular interactions. It is based upon the interaction of light with the chemical bonds within a material. Raman is a light scattering technique, whereby a molecule scatters incident light from a high intensity laser light source. Most of the scattered light is at the same wavelength (or color) as the laser source and does not provide useful information – this is called Rayleigh Scatter. However a small amount of light (typically 0.0000001%) is scattered at different wavelengths (or colors), which depend on the chemical structure of the analyte – this is called Raman Scatter.

A Raman spectrum features a number of peaks, showing the intensity and wavelength position of the Raman scattered light (Ranjan et al., 2021).

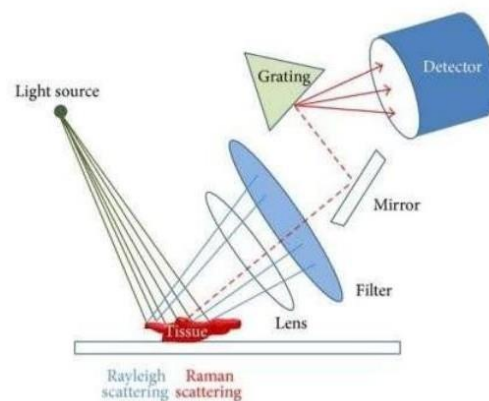


Fig5.3 The principle working of Raman spectroscopy

Hall Effect Measurement:

- +The electrical characteristics of semiconductors, such as CZTS (Copper Zinc Tin Sulphide), a potential material for thin-film solar cells, can be measured using the method known as Hall effect measurement.
- Hall effect measurement is an effective method for describing the electrical characteristics of CZTS thin films and can offer crucial insights for the creation of high-performance thin-film solar cells.

- The charge carrier concentration, mobility, and conductivity of the material all crucial aspects that affect the solar cell's performance can be learned through Hall effect measurements in CZTS thin-film solar cells.
- An electric current is sent through the sample while a magnetic field is applied perpendicular to the sample surface to measure the Hall effect. The resulting voltage, which relates to the Hall coefficient a measure of the mobility of the charge carriers in the material is measured. The carrier concentration and conductivity of the material are inferred from the Hall coefficient, which is calculated.
- It is possible to optimise the method of production for high carrier concentration and mobility, which are essential for generating high solar cell performance, by conducting Hall effect measurements on CZTS thin films (Vanalakar et al., 2015).

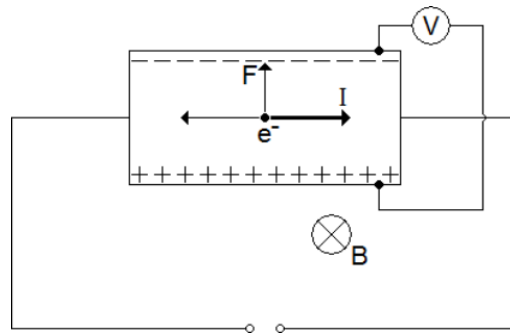


Fig5.3: The measurement of the hall effect in a bar sample carrying electrons

CHAPTER 6

RESULTS AND DISCUSSION

6.1.X-Ray Diffraction:

X-ray diffractograms of films is depicted in Peaks corresponding to the (1 1 2), (2 0 0), (2 2 0), (3 1 2) planes of CZTS could be observed. These are characteristic of the 'kesterite' structure of CZTS. For both the films, preferential orientation was along the (1 1 2) direction. Crystallite size (D) was determined using Debye Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

where λ is the wavelength of Cu K α line, β is the FWHM in radians and θ is the Bragg angle.

From the XRD peaks, lattice constants were calculated. CZTS has tetragonal structure, so the lattice constants are calculated as a and c .

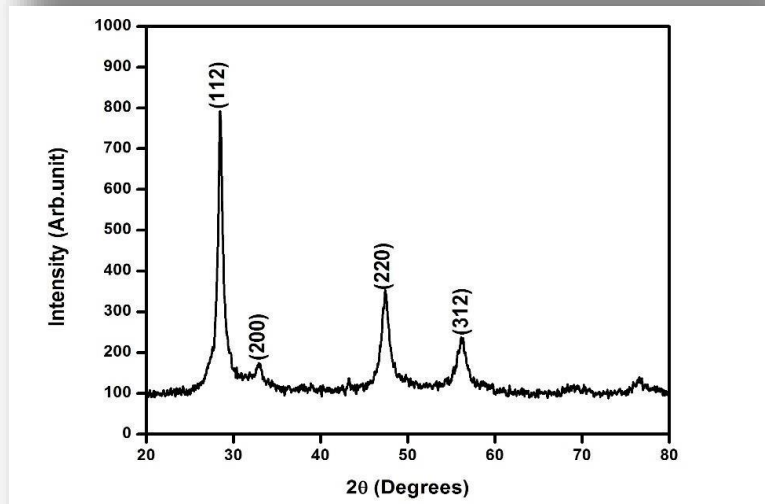


Fig 6.1: The XRD of CZTS

The above XRD pattern 2 θ is compared with JCPDS (26-0575) of the respective material. The observed diffraction data are in good agreement with the standard 2θ values of kesterite CZTS.

6.2. UV-Visible spectroscopy:

UV Spectroscopy is performed on the CZTS sample at room temperature. The formation of CZTS Compound was confirmed by the results.

The light sensitivity system that we observed for the CZTS cannot handle CdS, which has a high resistance under UV.

UV generally has the graph between reflectance and Transmittance along with the angle of diffraction(Agawane et al., 2015).

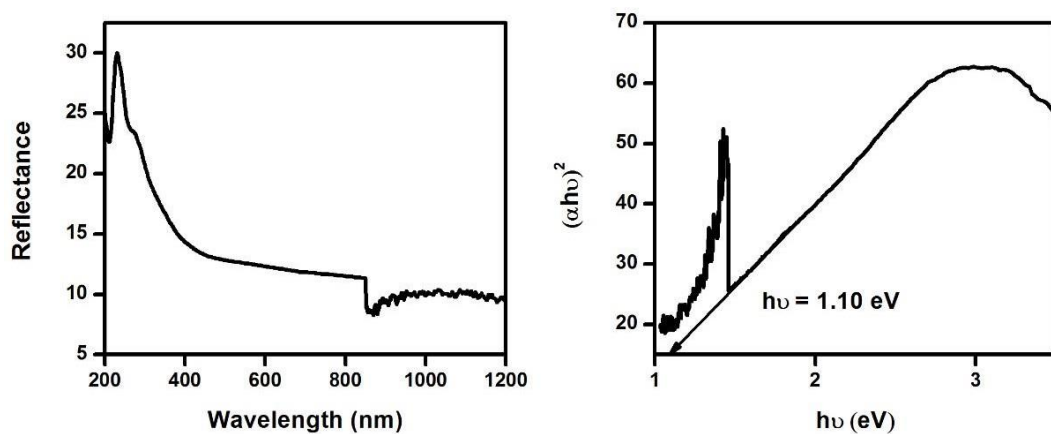


Fig 6.2: The UV graph of CZTS according to the reflectance

6.3. Hall effect measurement:

As we have discussed about the Hall Effect Measurement in detail, we came to know properties like conductivity, charge carrier concentration. The below graphs was observed at Room Temperatures

Compound	Current (A)	Bulk concentration (cm ⁻³)	Resistivity (ohm.cm)	Conductivity (mho.cm)	Mobility (cm ² v ⁻¹ s ⁻¹)	Average hall coefficient
CZTS	1×10 ⁻³	1.91×10 ¹⁹	9.44×10 ⁻³	1.06×10 ²	34.6	0.326

Table 6.1 Hall effect measurement

6.4 Raman spectroscopy:

Fig (6.3) clearly shows a strong peak at 333 cm^{-1} which corresponds to the main features of the vibrational A_1 symmetry mode of CZTS. In addition, we observed a broad peak at 292 and 365 cm^{-1} which are close to the values reported for CZTS.

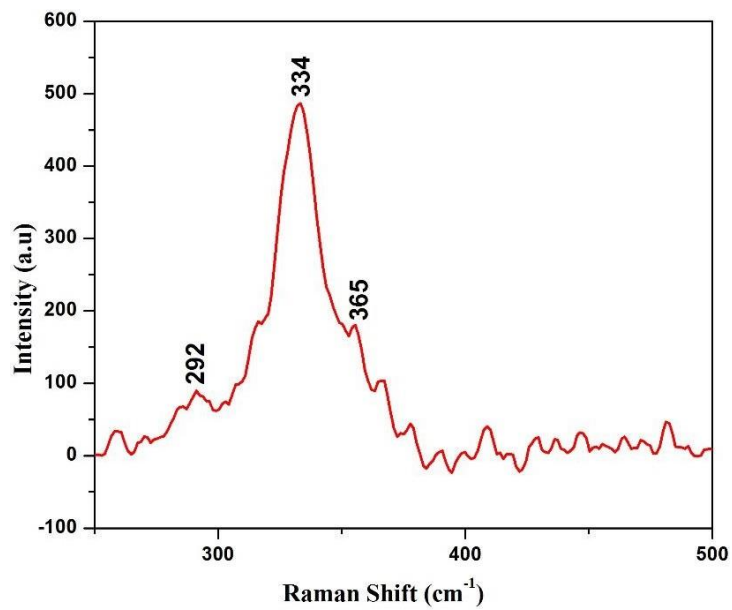


Fig6.3: The Raman shift graph of CZTS thin film

CHAPTER 7

CONCLUSION:

We have developed II-VI group thin-film solar cells on glass substrates in order to promote low-cost, environmentally friendly, and long-lasting solar energy devices. CdS thin film is a potential candidate for a window layer. A p-type CZTS material were successfully synthesized by ball milling at different milling time in the ratio of 2:1:1:4. Then it was thermally evaporated on a glass substrate at Room Temperature (RT) and various temperatures. The structure of prepared CZTS nanocrystals is determined by XRD, with a cubic structure (112) plane as the preferred orientation. Thickness was also measured using thickness profilometer for different temperature. The deposited films were subjected to UV- Visible spectroscopic studies. From the reflectance the materials show its suitability for reflecting and anti-reflecting coatings. The electrical properties reveal the measure of carrier concentration and mobility with respect to the variation in current input. The above studies show the synthesized and thermally evaporated CZTS as a potential candidate for solar cell applications.

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