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Characterization of large area cadmium telluride films and solar cells deposited on moving substrates by close spaced sublimation

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Characterization Of Large Area Cadmium Telluride Films And Solar Cells Deposited On
Moving Substrates By Close Spaced Sublimation

by

Vishwanath Kumar

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science in Electrical Engineering
Department of Electrical Engineering
College of Engineering
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Dedication

I would like to dedicate this thesis work to my parents for their love, support and unduly faith in me.
I wish to thank Dr. Chris Ferekides for his guidance and continual support during the course of my efforts to complete this work. I would also like to thank Dr. Don Morel for his insights, comments and timely counsel. I would also like to thank Dr. Y. L. Chiou for his technical assistance during my graduate program.

Special thanks to my fellow colleagues, especially to Mr. Su Yu, who is my good friend, inspiration, guide and mentor. I would also like to thank my sister and also my friend Thanigainathan for their encouragement and support.
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Characterization Of Large Area Cadmium Telluride Films And Solar Cells
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Vishwanath Kumar

ABSTRACT

With CdTe based photovoltaics developed by close spaced sublimation reaching efficiencies of over 16%, commercialization of this technology draws serious attention. Today large area industrial modules have not been able to produce the same performance of their laboratory counterparts. This work provides a means for understanding the various technical challenges in developing an effective deposition technology for large area processing.

The submodule process investigated provides a model for continuous and sequential processing of subsequent films. The system has a unique design and constructed with the provision for a moving transport module for the substrate transport. The process was developed to deposit large area CdTe (3 x 3 sq. inch) and provides valuable insights for the development of a large area deposition system.

Upon optimizing the system for reproducibility, proper deposition conditions were established. Films deposited under various conditions were studied to improve our understanding of the influence of processing conditions on device performance. The key advantage of this technique over others is its high deposition rate, simplicity of operation and high conversion efficiency. Typical deposition times were two minutes and could be reduced to as low as 45 sec with little variation in performance.
The four major parameters that influence the films prepared by close spaced sublimation, namely substrate temperature, source temperature, ambient pressure, and spacing were optimized for best device performance. The influence of each parameter on deposition rate and cell efficiency was also studied.

The best cells produced by this technology had an efficiency of 13% with $V_{oc}=830\, \text{mV}$, $FF=74\%$ and $J_{sc}=21.1\, \text{mA/cm}^2$. 
Chapter One
Overview of Solar Cells

Direct conversion of sunlight into electricity using the photovoltaic properties of suitable materials, is the most promising energy conversion system. During the last three decades, the solar cell technology has enormously developed for both space and terrestrial applications. It is realized that the conventional fossil energy resources such as oil, gas and coal are not only limited, but they will also contribute to irreversible climate changes in the near future through the emission of greenhouse gases like carbon dioxide to the atmosphere. The environmental pollution problems in developed and developing countries have been of immense concern. The use of sunlight offers a conceivable alternative energy source to the world energy and environmental problems.

Solar cells work on the principle of photovoltaic effect, discovered in 1839 by Henri Becquerel. The research in solar energy gained substantial significance only after Einstein’s explanation to photoconversion based on the theory of quantized photons. For the prevalent utilization of solar energy to become a reality, scientists have to develop more efficient solar energy conversion devices while lowering the costs at the same time. Identifying ideal photovoltaic materials with high conversion efficiency and development of inexpensive manufacturing technologies will play a key role in determining the acceptance of solar power as global solution for alternate energy.

Numerous materials have been investigated for solar cell applications. This lead to the development of new and innovative classes of semiconductor devices: Crystalline
silicon, amorphous silicon and thin film polycrystalline materials like cadmium telluride, copper indium diselenide etc. The choice of the material for solar cells depends upon the potential conversion efficiency expected from the devices made from them. It is found that for maximum conversion efficiency, the bandgap of the material should be approximately 1.5 eV. CdTe with a bandgap of 1.45 eV is the leading material for solar cell fabrication. Being a direct bandgap semiconductor, CdTe have as a very high absorption coefficient. A CdTe film of a micron thick can absorb 90% of the solar spectrum. CdTe has the flexibility to be deposited by a number of deposition techniques. Close spaced sublimation has been the most productive method owing to the very high deposition rate, low material consumption and low cost of operation. Moreover the devices with maximum conversion efficiency ever achieved in the laboratories were produced by this technique.

The main objective of this work is to characterize a system to produce large area CdTe (3 x 3 sq. inch) solar cells by close spaced sublimation. The work involves simulating a module fabrication process where in the substrates (3 x 3 sq. inch) are moved in batches over heated source. Characterizing involves scaling the size of the devices with acceptable uniformity, low material consumption, high deposition rates and appreciable device parameters. This could serve as a means to study the issues concerned with production of large scale industrial modules.

1.1 Solar cell

A solar cell is photovoltaic device that converts light energy into electrical energy. It is just a p-n junction diode that conducts current when incident upon by light.
The radiation from the sun provides the earth with an enormous amount of energy. With the use of solar cells we can convert some of this energy directly into electricity. In this chapter a brief introduction to the solar spectrum, the principle of photovoltaic effect and the basic operation of the solar cells will be discussed.

1.2 Solar spectrum

To study the conversion efficiency of the solar cell, the knowledge of the exact spectral distribution of the sun is important.

![Solar Spectrum](image)

Figure 1. Solar spectrum
The total energy per unit area integrated over the entire spectrum and measured outside the earth’s atmosphere and perpendicular to the sun is a constant and is called the solar constant or air mass zero (AM 0). The spectral distribution undergoes considerable changes as the radiations pass through the atmosphere. Because of reflection, scattering, and absorption of light by gases and aerosols in the atmosphere, the intensity of this radiation is attenuated by at least 30%. The radiant power as seen at the surface of the earth is called AM 1.5. It is the solar spectral irradiance distribution (diffuse and direct) incident at sea level from the sun-facing a 37-degree tilted surface [21]. Figure 1 gives a spectrum for global and direct irradiance of the sun. The spectral distribution for an AM1.5 with a total power density of 0.844 kW/m² [22] is adopted as the standard for terrestrial applications.

1.3 Photovoltaic effect

The "photovoltaic effect" is the basic physical process through which a solar cell operates. Sunlight is composed of photons, or discrete units of light energy. These photons contain various amounts of energy corresponding to the different wavelengths of light. When photons strike a PV cell, some are absorbed by the semiconductor material and the energy is transferred to electrons. With this new-found energy, the electrons can escape from their associated atoms and flow as current in an electrical circuit. Band gap energy is defined as the amount of energy required to dislodge an electron from its covalent bond and allow it to become a part of an electric circuit. Photons with energy higher than the band gap energy will be absorbed to generate electrons-hole pairs and the extra energy will be dissipated as heat. Photons with energy less than the band gap energy
will have no contribution to the junction output. Figure 2 depicts a simple photovoltaic reaction where the incident photon causes an electron hole pair (exciton) to be generated. Minority carriers—that is, electrons in the p material and holes in the n material created in sufficient quantities lower the potential energy barrier at the junction, allowing current to flow and establish a voltage at the external terminals. Thus photovoltaic effect is a chain reaction which involves light absorption, exciton creation, exciton diffusion, charge separation, and charge collection.

![Photovoltaic effect diagram](image)

**Figure 2. Photovoltaic effect**

### 1.4 PN junction

In its simplest form, the solar cell consists of a junction formed between n-type and p-type semiconductors, either of the same material (homojunction) or different
materials (heterojunction) [1]. When the two halves are brought together, the Fermi levels on either side are forced into coincidence, causing the valence and conduction bands to bend.

Free electrons from the n-type semiconductor diffuse into the p-type semiconductor and the holes diffuse from the p-type semiconductor into the n-type semiconductor. This movement of charge carriers is called the diffusion current. As the diffusion current flows, static charges build up in both p-type and n-type materials close to the junction. This charged area is called the space charge region. The charged areas form a potential difference, inducing a current to flow. This current is called the drift current. It flows in the opposite direction to the diffusion current, and consists of
electrons moving from the p-type semiconductor towards n-type semiconductor. As the same time, holes move from n-type towards the p-type material. Figure 3 shows a typical band energy diagram of an illuminated pn junction.

1.5 Fundamental solar cell parameters

A positive voltage applied to the p side relative to the n side causes current flow across the junction. Conversely, a negative voltage applied to the p side relative to the n side causes the space charge region to widen thereby blocking the current flow. The former condition is referred to as forward bias and the latter as reverse bias. These diode characteristics are best described the ideal diode equation given by

$$I = I_0 \left( \exp \left( \frac{qV}{AkT} \right) - 1 \right)$$

Where $I$ is the external current flow, $I_0$ is the reverse saturation current, $q$ is the fundamental electronic charge of $1.602 \times 10^{-19}$ coulomb, $V$ is the applied voltage, $k$ is the Boltzmann constant, and $T$ is the absolute temperature.

Figure 4. Equivalent circuit for a solar cell
Figure 4 is a model of a photovoltaic device. It represents an ideal diode in parallel with a light-induced current source. $R_s$ and $R_{sh}$ represent the series and shunt resistance respectively. In practice the actual voltage applied to the device does not entirely appear across the junction. The voltage drop across the external contacts causes ohmic losses. This is represented by the series resistance. Thus the series resistance is due to the bulk resistance of the semiconductor and the resistance of the contacts and interconnections. The losses due to leakage currents and extended lattice defects are represented by the shunt resistance [4].

![Figure 4](image)

Figure 5. (a) IV characteristics of solar cell in the dark and when illuminated. (b) Maximum power rectangle.

The current and voltage characteristics equation for an illuminated pn junction is given by

$$ I = I_0 (\exp(qV/kT) - 1) - I_L $$

------- (2)
Rewriting equation (2) after incorporating $R_s$ and $R_{sh}$

$$I = I_o \left( \exp \left( \frac{q(V - IR_s)}{AkT} \right) - 1 \right) + \left( \frac{VR_s}{R_{sh}} \right) - I_L \quad \text{------ (3)}$$

A schematic of an I-V curve showing dark and illuminated junctions is shown in figure 5. When the diode is illuminated, the dark current characteristic shifts down by $I_L$. The product $I$-$V$ is negative implying power output. The curve describes three important parameters that give complete description of the solar cell: short circuit current ($I_{SC}$), open circuit voltage ($V_{OC}$) and fill factor (FF).

Short circuit current ($I_{SC}$) is obtained when the voltage drop across the junction is zero. This means that under ideal conditions $I_{SC}$ is $I_L$. However $I_{SC}$ will be lower than $I_L$ due to the effect of series and shunt resistances. Open circuit voltage ($V_{OC}$) is obtained when $I = 0$.

$$V_{OC} = \frac{kT}{q} \ln \left( \frac{I_L}{I_s} + 1 \right) \quad \text{------ (4)}$$

The conversion efficiency is a measure of the performance of a solar cell. This is determined by the maximum output power of the device. This is equal to the area of maximum power rectangle, shown in figure 5.

$$P_{\text{max}} = I_m \times V_m \quad \text{------ (5)}$$

The ratio $P_{\text{max}}/ I_{SC} \times V_{OC}$ is called Fill Factor.

$$\text{FF} = \frac{I_m \times V_m}{I_{SC} \times V_{OC}} \quad \text{------ (6)}$$

Thus conversion efficiency of a solar cell is given by

$$\eta = \frac{P_{\text{out}}}{P_{\text{in}}} \quad \text{------ (7)}$$
The terrestrial standard of $P_{in}$ is 100mW/cm$^2$.

1.6 Quantum efficiency

For an ideal solar cell, every incident photon would generate an electron-hole pair, and each of the photo carriers would make it to the depletion region where they could be separated and collected. Photons with energy less than the bandgap have insufficient energy to generate photo-carriers. Even if it has the sufficient energy, it need not contribute to the photocurrent. Quantum efficiency of a photon of wavelength $\lambda$ is the probability that the photon contributes an electron to the photocurrent. It is the measure of the effectiveness of a device to produce electronic charge from incident photons. Quantum efficiency (Q.E.) describes response of the device to different wavelengths of light.

$$Q.E.(\lambda) = \frac{1}{q} \frac{hc}{\lambda} \frac{I_{sc}(\lambda)}{P(\lambda)}$$

where $q$ is the unit charge, $\lambda$ is the photon wavelength, $h$ is Planck’s constant, $c$ is the speed of light in air, $I_{sc}(\lambda)$ is the short circuit current and $P$ is incident light power. The QE is expected to be zero for photons with energy less than the absorber bandgap. For photons with a larger energy, the QE can be as large as 100% but is often lower. There are several reasons for this. First, there is a probability that the photon is reflected at the top interface and never enters the solar cell. Secondly, many photons that enter the top of the cell get adsorbed in the upper layers, never reaching the absorber layer below. This is true for heterojunctions and photons with energy larger than the band gap of the
transparent conducting oxide (TCO) and window layer. The TCO is the transparent front contact for the solar cells and the window layer is the large bandgap heterojunction partner for the absorber. Third, even if a photon reaches the absorber layer with sufficient photon energy, the photo carriers can recombine before they enter the depletion region where they are separated to become a part of photocurrent.

1.7 CdTe thin film solar cells

The quest to produce truly low cost solar cells was quenched with the advent of thin film photovoltaics. Over the years, research and development have demonstrated CdTe based solar cells to be a strong candidate to set the standard for next generation solar cells. Recently NREL has developed CdTe solar cells with efficiency of 16.4% [23]. Figure 6 shows some of the highest efficiencies achieved on CdTe solar cells. With sufficient progress in process technology, CdTe solar cells can make sufficient inroads into a dominant position in commercial production.
Figure 6. Highest efficiencies achieved on CdTe solar cells
Chapter Two
Processing of Cadmium Telluride

Developing an effective manufacturing process for module fabrication requires easily scalable, high throughput techniques with the potential to yield high efficiency devices. Understanding the complex issues of film properties, junction formation and how these are affected by processing is crucial for successfully converting laboratory processes into a manufacturing process. A technique with high deposition rate, low cost and a potential for high conversion efficiency will be make a good candidate for manufacturing purposes.

One of the greatest advantages of CdTe photovoltaic technology is the freedom it provides with respect to its method of deposition. A lot of these techniques have given efficiencies of over 12%. However there is a gap between efficiencies of laboratory cells and PV modules. So a better understanding of the effect of processing on the cell performance is very essential. To assess processing options for CdTe it is necessary to understand the material and determine the critical properties needed in the thin film and other parts of the device structure. The next step is to understand the deposition and processing techniques and determine if they have the capability of providing the critical properties needed in the various layers without apparent limitations. Finally, the reproducibility and uniformity must be assessed and means for process control developed. Different deposition techniques for CdTe include close spaced sublimation (CSS), electrodeposition, screen printing, spraying, chemical vapor deposition (CVD),
evaporation, sputtering, laser driven PVD and molecular beam epitaxy (MBE). In all cases, sufficient deposition rates have been demonstrated so that, at least in batch mode, large throughput is feasible.

2.1 Cadmium Telluride

![Structure of cadmium telluride](image)

Figure 7. Structure of cadmium telluride

Of the II-IV semiconducting photovoltaic materials available, cadmium telluride has good optical performance across a wide range of temperatures and has provided adequate mechanical robustness to be used as a substrate material. Compared to the limited selection of alternative materials, CdTe has a high resistance to moisture sensitivity and is available at a reasonable price. It has a cubic zincblende structure with a lattice parameter of 6.481 Å and a density of 6.2 g/cm³. It has a thermal coefficient of expansion of 4.9x10⁻⁶ K⁻¹ and electron affinity of 4.3 eV. It has a melting point of 1040
A. P type CdTe has a very high work function of 5.5 eV. One special property of CdTe is that it can be doped both as p-type as well as an n-type material.

CdTe is a direct bandgap semiconductor material with an energy gap of 1.45 eV and is therefore well suited for efficient conversion of solar light into electricity. It has a very high absorption coefficient for visible light of over $10^4$ cm$^{-1}$ [4] and hence only a micron thick CdTe can absorb over 90% of photons with energy greater than 1.45eV. CdTe is stable for temperatures of up to 500 °C. Being a defect semiconductor, CdTe has native defects [4]. The cation vacancies ($V_{\text{Cd}}$) can act as double acceptors while anion vacancies ($V_{\text{Te}}$) are double donors. In addition, complexes of these vacancies can be formed with other extrinsic impurities. CdTe still continues to be a leading contender as an absorber material for thin film photovoltaic applications. Today, close spaced sublimation is the most effective technique for CdTe heterojunction solar cell fabrication.

2.2 Processing techniques

2.2.1 Electrodeposition

Electrodeposition is the process where an electric current is passed through an electrolytic solution or other appropriate medium, causing a chemical reaction. This results in the deposition of a substance on the cathode from a solution of its ions.

R.K. Sharma et. al deposited CdTe thin films electrochemically from an acidic aqueous solution containing 2.5 M CdSO$_4$·8H$2$O and 120 ppm TeO$_2$ [4]. Deposition temperature was kept constant to 80 °C. Electrolytic bath was kept under constant stirring of about 60–70 rpm. Saturated Calomel electrode (SCE) was used to determine the CdTe
deposition conditions and maintained at 0.58 to 0.62 V. Electronic grade H₂SO₄ was used to ensure the availability of H⁺ ions during deposition and the pH was maintained at about 2. The electrochemical cell containing platinum was the anode, saturated Calomel as the reference electrode and the CdS coated substrate was the working electrode. Typical growth rates are about 0.86 µm/hr.

2.2.2 Screen printing

Screen printing is a commonly used industrial technique for fast, inexpensive deposition of dye films over large areas. From this standpoint, it is an ideal technology for large scale fabrication of polymer based solar cells. In addition, screen printing allows patterning to easily define which areas of the substrate receive deposition. This is important, for instance, for fabricating a photovoltaic device that is integrated onto a substrate containing other electronic devices. Also, in the production of a large area energy collection system, it is necessary to fabricate many individual solar cells that are wired together. Using screen printing, individual devices can easily be defined on the same substrate in order to optimize the power generation of the entire system.

CdTe can be deposited by screen printing either from a mixture of Cd and Te powder or from CdTe powder [9]. Solveig Roschier et.al prepared CdTe powder from a slurry consisting of CdTe powder with 5 wt% of CdCl₂ and an appropriate amount of propylene glycol (PG) was prepared by mixing and dispersing with a mortar and pestle. The slurry was coated on borosilicate glass substrates using a screen printer with a mesh silk screen to obtain a CdTe layer. After the CdTe layer was dried, the CdTe layer was sintered at 625 °C for 1 hour in nitrogen. CdTe can also be deposited from slurry
consisting of (Cd + Te) mixture in an appropriate Cd/Te ratio. Then the dried CdTe layers were pushed slowly into a tube furnace at the rate of 14°C/min up to 500°C in nitrogen. The use of Cd + Te powder leads to the elimination of sintering procedure. XRD analysis showed that only the CdTe phase existed in the deposited layers. Although this technology is cost effective, developing a convenient and reproducible procedure is difficult. As compared to other technologies, screen printing usually leads to thick layers (10-20 μm) and requires rather high fabrication temperatures.

2.2.3 Sputtering

Sputtering is a physical vapor deposition (PVD) technique [10] used for precision coatings of thin films in vacuum. The substrate is placed in a vacuum chamber with a target of the material to be deposited. Plasma is generated in a passive source gas like Ar in the chamber, and the ion bombardment is directed towards the target, causing material to be sputtered off the target and condense on the chamber walls and the substrate. Sputtering can either be RF or DC. A strong magnetic field (magnetron) can be used to concentrate the plasma near the target to increase the deposition rate. The deposition rate depends on the pressure, gas flow rate, RF power, substrate temperature and target-substrate spacing. Growth rates were typically 3 Å/sec.

Laser driven physical vapor deposition (LDPVD) has been employed to achieve slightly higher deposition rates and also to improve the material quality of the deposited films. A focused laser beam is directed at the target surface. A planar target is rotated or (x, y) - scanned in the focal plane of the laser beam to achieve a steady ablation rate. The substrate located at a typical separation from the target is held stationary or is rotated for
homogenization of the deposition rate. Advantages of the LDPVD method over other deposition techniques include the unique process of source material transfer which limits the amount of heated material virtually only to that which is liberated. Its pulsed nature affords high controllability of the deposition thickness. The high kinetic energy of the ablation promotes surface mobility on the growing film. There appear to be certain drawbacks associated with LDPVD. Foremost of these are inhomogeneities of deposition rates, pulse-to-pulse fluctuations in the laser intensity and possible nonstoichiometric material transfer of multi-elemental targets. These problems arise not only from material specific properties, but also from technological limitations and an incomplete understanding of the control parameters. Moreover it is an expensive process.

2.2.4 Atomic layer epitaxy

Atomic layer epitaxy (ALE) is a technique where components coming from elemental sources are deposited alternatively onto a growing surface. It is based on sequential chemical reactions on the surface [9]. It is suitable for the deposition II-VI thin film. Characteristics of thin films produced by ALE are good crystallinity, excellent uniformity over a large area and low pinhole density. Laboratory of advanced energy systems, Finland used ALE to grow both CdS and CdTe layers in a single process. Low pressure type ALE reactor is based on reactant transport and valving with computer controlled inert gas flow. The reactor was equipped with four individually controlled sources for solid reactants inside the reactor body and a definable number of external sources for gas and liquid reactants. The reaction zone consists of a 1-3 mm space between two 50 x 50 mm$^2$ substrates. The lateral flow through the reaction zone ensures
an effective reactant/substrate interaction resulting in high material efficiency. Cadmium sulphide films were grown using elemental Cd and S as reactants. A possible process temperature range is 300–500 °C. CdTe layers are grown in the temperature range between 350 °C and 440 °C using elemental Cd and Te as reactants. All the layers were processed in one run and at the same reaction temperature. To minimize the effects from the lattice mismatch between CdS and CdTe on the electrical function of the heterojunction, a graded layer is processed between CdS and CdTe in which the CdS/CdTe proportion was gradually changed from pure CdS to pure CdTe.

2.2.5 Chemical vapor deposition

2.2.5.1 Metal organic chemical vapor deposition (MOCVD)

Chemical vapor deposition (CVD) is the process of chemically reacting a volatile compound of a material to be deposited, with other gases, to produce a nonvolatile solid that deposits atomistically on a suitably placed substrate. Of the various types of CVD process, MOCVD, also known as OMVPE (organometallic vapor phase epitaxy) has assumed considerable importance in the deposition of epitaxial compound semiconductor films.

CdTe can be deposited on glass at substrate temperatures of 350-400 °C by the reaction between DiMethylCadmium (DMCd) and Diisopropyltellurium (DIPTe) in hydrogen atmosphere [4]. Typical flow rate of hydrogen and DIPTe was about 4.5 liters/min and 3.6 x 10^{-5} mole/min respectively. The flow rate of DMCd was such that it yields DMCd/DIPTe molar ratio of 0.34 - 2. The deposition rates were about 4.3 µm/hr at typical conditions.
(CH₃)₂Cd + (C₃H₇)₂Te + H₂ → CdTe + 6 CH₄

Safe handling of the gases employed in CVD systems is a concern of paramount importance. As the reactant and product gases can be toxic, flammable, or corrosive and mostly possess a combination of the above attributes, they are less accepted as the foremost processing option.

2.2.5.2 Atmospheric pressure chemical vapor deposition (APCVD)

APCVD of polycrystalline thin film CdTe appears to offer several practical advantages over state-of-the-art manufacturing techniques. APCVD combines the proven reaction chemistry utilized to produce 16% efficient CdTe cells (i.e., same reaction chemistry as close spaced sublimation), allows for physical separation of the source and substrate, and employs forced convection to ensure uniform delivery of source material over large-area substrates.

APCVD's anticipated advantages for manufacturing environments include:

1. Low equipment cost compared to vacuum processing because the equipment will need neither the structural strength nor the pumping systems of a vacuum chamber.
2. Large area uniformity can be achieved through control of temperature and gas flow, both of which are subject to rigorous engineering design.
3. Process control and source replenishment are simplified because the source gas generation is physically separated from the deposition chamber.
4. Process compatibility attained in APCVD is excellent. In fact, the processing sequence: deposit TCO, deposit CdS, deposit CdTe, dry CdCl₂ heat treatment and
metal organic CVD of electrodes could be performed in a single continuous process.

5. Raw material costs are low as CdTe is used in its least expensive form as chunks. The deposition rates achieved are about 0.2µ/min.

### 2.2.6 Chemical spray pyrolysis

In chemical spraying an aerosol of water droplets containing heat decomposable compounds of Cd and Te is sprayed onto a heated substrate forming a CdTe film [9]. In a large area CdS/CdTe prototype module based on spray pyrolysis, 0.5 – 1.2 µm tin-oxides was deposited on commercial 3-mm float glass. The deposition temperature was 480 °C. A CdS film of 6 µm thickness was deposited on top of the tin oxide and subsequently 6 µm of CdTe was deposited onto the CdS. CdTe was made conductive with phosphorus. After bromine/methanol etch and subsequent NaOH soak to remove the surface oxide, a graphite electrode was deposited on top of the CdTe to a thickness of 10 µm. A more-conductive electrode containing tin was evaporated on top of the structure to complete the device. Devices produced by this method had efficiencies of about 10%.

### 2.2.7 Evaporation

Evaporation is a physical vapor deposition technique where the material to be deposited in the solid form is heated until evaporation.

Polycrystalline CdTe films have been deposited onto glass substrates at 373K by the evaporation technique in a vacuum higher than $10^{-6}$ torr under controlled growth
conditions. The thicknesses of the films were controlled by using a quartz crystal thickness monitor. The source to substrate distance was kept a constant (10 cm) and substrate was kept at constant temperature (373 K). The deposition rate was around 10 – 15 Å/sec.

As evaporation is operated in high vacuum, the evaporated atoms reach the substrate without any intervening collisions. Although the deposited layer is very pure, the film properties are difficult to control. Evaporation suffers from poor uniformity and large shadowing effects. Hence scaling up is very difficult. It may also have poor stoichiometry.

### 2.2.8 Molecular beam epitaxy

Scientists can build layers of atoms one onto another using a method called Molecular Beam Epitaxy (MBE). MBE means “building a crystal structure on top of another with streams of molecules or atoms” [12].

MBE was developed in the early 1970s as a means of growing high-purity epitaxial layers of compound semiconductors. It is a popular technique for growing III-V compound semiconductors as well as several other materials. MBE can produce high-quality layers with very abrupt interfaces and good control of thickness, doping, and composition. Because of the high degree of control possible with MBE, it is a valuable tool in the development of sophisticated electronic and optoelectronic devices.

In MBE, the constituent elements of a semiconductor in the form of ‘molecular beams’ are deposited onto a heated crystalline substrate to form thin epitaxial layers. The ‘molecular beams’ are typically from thermally evaporated elemental sources, but other
sources include metal-organic precursors (MOMBE), gaseous hydride or organic precursors (gas-source MBE), or some combination (chemical beam epitaxy or CBE). To obtain high-purity layers, it is critical that the material sources be extremely pure and that the entire process be done in an ultra-high vacuum environment (10^{-11} torr). Another important feature is that growth rates are typically on the order of a few angstroms per second and the beams can be shuttered in a fraction of a second, allowing for nearly atomically abrupt transitions from one material to another. Typical growth rates are about 1\mu m/hr. Major disadvantage of this process is that it is very expensive.

2.2.9 Close spaced sublimation

Close spaced sublimation (CSS) is the process where crystals and films of electronic material containing components of different volatility are prepared by sublimation of the source material and condensation of the resulting vapor on the substrate that is placed in closed proximity above the source [4].

The CSS of CdTe is based on its reversible dissociation of CdTe at high temperatures.

\[
\text{CdTe} \xleftarrow{\triangle} \text{Cd} + \frac{1}{2}\text{Te}_2
\]

In this technique, the substrate is placed just above a CdTe source in a closed reactor. They are then heated simultaneously by an external source, maintaining a constant temperature difference between the two. The deposition is carried out in an ambient of He, O\textsubscript{2}, H\textsubscript{2} or Ar or a combination of two or more of these reactant gases. The main advantage of CSS over other processes is its high deposition rate (upto 10\mu m/min).
Based on a detailed investigation of closed spaced sublimation of CdTe, it is found that the material transport and hence the growth depends only on (1) the spacing between the source and substrate (2) source and substrate temperature (3) ambient pressure (4) composition of the source material.

2.2.9.1 Spacing

The spacing between the source and the substrate has to be an optimum affordable minimum. This would not only increase the deposition rate but also reduce the material consumption per deposition. It is desirable that nearly all the material consumed for the source is deposited on the substrate. The growth rate ($r$) varies inversely as the spacing ($h$) [13]. It is found that if the spacing is kept small, then the material transport is diffusion limited and the surface heat transfer can be conductive, radiative, and convective.

2.2.9.2 Substrate temperature

The substrate temperature is one of the most important parameter that determines not only the deposition rate but also the characteristic of the electrical junction formed at the CdS/CdTe interface. Upon extensive research, it has been found that CdTe deposited at high substrate temperatures exhibited better performance [16].

The deposition rate is greatly improved at higher substrate temperatures. For a variation of about 50 $^\circ$C, the deposition rate seems to be increase by times. And so do the
film density which increased with the deposition rate. A considerable reduction in grain size was also observed at high substrate temperatures.

An increase in substrate temperature leads to a decrease in the resistivity of the CdTe film [17]. It is concluded that most of the significant variation of resistivity is due to the oxygen partial pressure.

All these factors combine to increase the performance of the device. The devices made at high substrate temperatures have substantial increase in all of the solar cell parameters namely open circuit voltage (V_{OC}), Fill Factor (FF), short circuit current (I_{SC}), and hence the efficiency (\eta).

Figure 8. Effect of substrate temperature on (a) V_{OC} and FF (b) resistivity and grain size [17]
2.2.9.3 Annealing temperature

Annealing of CdS films in the presence of H₂ has been found to influence the film properties and hence the performance. This is done just before the deposition of CdTe as it improves the mobility of the films [15]. Increasing the annealing temperature seems to increase the $V_{OC}$ and spectral response behavior. Increasing the annealing temperature enhances the spectral response in the 500-600nm region. Another aspect of thermal annealing is that it reduces the surface roughness of the CdS layer which could reduce the recombination centers around the junction [14]. Hence an improvement in the cell efficiency was observed.

2.2.9.4 Effect of oxygen partial pressure

The presence of O₂ enhances the p-type characteristics of CdTe, improves the CdTe coverage, decreases the pinhole density and improves the junction quality. The resistivity of the samples decreased with partial pressure of oxygen [17]. Presence of O₂ decreases the sublimation rate of CdTe. Films grown in the presence of O₂ have smaller grains. Back lighting studies of these films show that the films are free of pinholes [19]. O₂ has certain drawbacks. It oxidizes the CdTe source non-uniformly. The graphite boat containing the CdTe source may react with the O₂ to form CO and CO₂.

2.2.9.5 Growth rate

The unique advantage of close spaced sublimation of CdTe is the high deposition rate that could be achieved without any changes in the optical and electrical properties of
the deposited films. Thus achieving an acceptable deposition rate from optimum conditions of temperature, pressure, spacing etc is necessary. A theoretical understanding of the deposition rate [12] with respect to the above parameters will provide substantial support for the experimental conclusions.

Close spaced sublimation of CdTe is a diffusion limited model. The transport of CdTe is considered to occur via reaction (11) and is considered to be dependant only on the following five factors.

1. Substrate temperature (T1)
2. Source temperature (T2)
3. Spacing between source and the substrate.
4. Source stoichiometry.
5. Pressure in the reaction chamber

The diffusive flux is given by Fick’s first law

\[
J = -D_i \frac{dC}{dx}
\]

Where \( D_i \) is the diffusivity of the solid, \( dC/dx \) is the concentration gradient of the vapor.

Ideal gas law states

\[
C = \frac{P}{RT}
\]

Substituting (13) in (12)

\[
J = -\frac{D_i}{RT} \frac{dC}{dx}
\]

Mass is transferred from the source to a substrate placed at a short distance, \( h \) above the source. Then integrating equation (11) over this distance,

\[
J = -\frac{D_i}{RTh} [P_{src} - P_{sub}]
\]
The equilibria at the source and the substrate temperature are represented by equation (16) and (17) respectively.

\[
[P_{cd}] [P_{Te}]^{1/2} = \exp \left( \frac{-\nabla G(T_1)}{RT_1} \right) \quad \text{(16)}
\]

\[
[P_{cd}] [P_{Te}]^{1/2} = \exp \left( \frac{-\nabla G(T_2)}{RT_2} \right) \quad \text{(17)}
\]

Based on the source stoichiometry,

\[
J_{cd} = 2J_{Te} \quad \text{(18)}
\]

Where the individual mass fluxes are given by

\[
J_{cd} = \frac{D_{cd}}{R_h} \left[ \frac{P_{cd}(T_1)}{T_1} - \frac{P_{cd}(T_2)}{T_2} \right] \quad \text{(19)}
\]

\[
J_{Te} = \frac{D_{Te}}{R_h} \left[ \frac{P_{Te}(T_1)}{T_1} - \frac{P_{Te}(T_2)}{T_2} \right] \quad \text{(20)}
\]

Then the growth rate is given by

\[
GR = A \cdot \frac{J_{cd}M}{\rho} \quad \text{(21)}
\]

Where \( M \) = molecular mass of CdTe, \( \rho \) is the density of CdTe and \( A \) is a constant.

Empirical equation for diffusivity

Elementary kinetic theory of gases predicts that the diffusion coefficient depends on the pressure and temperature as

\[
D = D_0 \left[ \frac{P_0}{T} \right]^{\frac{n}{T_0}} \quad \text{(22)}
\]

The value of \( n \) is found experimentally to be 1.8. \( D_0 \) is the value of \( D \) measured at standard temperature \( T_0 \) (273 K) and pressure \( P_0 \) (1 atm). Thus the empirical value of growth rate depends \( T \) as
GR $\propto \frac{T^{1.8}}{\rho h}$ ------ (23)

### 2.3 Comparison of CdTe deposition technologies

Table 1. Deposition rate and efficiencies achieved by various CdTe deposition techniques

<table>
<thead>
<tr>
<th>CdTe Deposition Process</th>
<th>Deposition rate</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Closed Space Sublimation</td>
<td>10 $\mu$m/min</td>
<td>16.4%</td>
</tr>
<tr>
<td>Molecular beam epitaxy</td>
<td>1 $\mu$m/hr</td>
<td>10.5%</td>
</tr>
<tr>
<td>Evaporation</td>
<td>15 Å/sec</td>
<td>11.8%</td>
</tr>
<tr>
<td>MOCVD</td>
<td>4.3 $\mu$m/min</td>
<td>11.9%</td>
</tr>
<tr>
<td>Electrodeposition</td>
<td>0.9 $\mu$m/hr</td>
<td>14.2%</td>
</tr>
<tr>
<td>PVD</td>
<td>3 Å/sec</td>
<td>10.5%</td>
</tr>
</tbody>
</table>
3.1 Cell structure

The CdS/CdTe solar cells are typically made in the superstrate structure configuration as shown in figure 3.1.

A thin layer of tin oxide (SnO$_2$), a transparent conducting oxide deposited by MOCVD on 7059 corning glass was used as the front contact. SnO$_2$ is deposited as a bilayer of an intrinsic layer on top of fluorine doped extrinsic layer. The SnO$_2$ layer has a sheet resistance of about 7 – 10 ohm cm$^2$.

Cadmium sulphide (CdS) is the most effective heterojunction partner for CdTe. With a bandgap of 2.42eV, CdS forms the window layer for these solar cells. Usually n-
CdS is solution grown by chemical bath deposition (CBD). The thickness of this layer is about 500 Å - 1000 Å and is highly conformal. The process is highly controllable as well as reproducible. CdS can also be deposited by CSS technique.

The CdS films are annealed in hydrogen ambient to improve the surface morphology. About 3 - 8 µm CdTe was deposited on CdS by close spaced sublimation. The samples are then treated with CdCl₂ to improve the device performance. Copper doped graphite paste was used as the back contact.

3.2 Close spaced sublimation of cadmium telluride

![Figure 10. Conventional CSS system](image-url)
Close spaced sublimation is the process where crystals and films of electronic material containing components of different volatility are prepared by sublimation of the source and condensation of the resulting vapor [4].

A deposition system used to produce small area CdTe solar cells is shown in figure 10. The source and the substrate are separated by two quartz spacers. A pair of graphite plates is used to hold the source and substrate in position. The source and substrate temperatures are measured inside these graphite blocks. All the above are enclosed in a quartz tube reactor. Halogen lamps used as the source for heating the source and the substrate. Vacuum is established by means of a mechanical pump. The source and substrate are heated in the presence of O\(_2\) and He such that the deposition rate is about 1µm/min. This technique has produced solar cells with efficiencies of above 15%.

This small area CSS system was used as the base for developing the large area technology. This stationary technique aided in understanding the processing details of the moving transport mechanism. The large area submodule developed is shown in figure 11. This system uses a turbo pump which is capable of high vacuum of about 10\(^{-8}\) torr. The vacuum pressure is measures using baratrons for the lower range and ion gauges for the higher range of vacuum. Three heaters are used: one for heating the source (H3), one for heating the substrate during deposition (H2) and a third for annealing/pre-heating prior to CdTe deposition (H1). The heaters are held in position by molybdenum frames. The heaters shielded by reflective molybdenum sheets in the rear side. K-type thermocouples were used. The substrate temperatures are read from the substrate heaters. The source temperature is read from the graphite boat containing the sintered CdTe source. The heaters are controlled by three Eurotherm controllers.
Figure 11. Large area close spaced sublimation system with moving substrate technology
The substrate is placed on a moving transport system. The transport system was mounted on a shaft which is driven by a stepper motor. The stepper motor was coupled to a computer by a VP 9000 Velmex controller. Precise control of the transport mechanism was established. The gas inlets are pneumatically actuated.

### 3.3 Experimental procedure

The CdTe source is made by sintering 99.9999% pure CdTe powder in H₂ ambient at a temperature of 650 °C – 800 °C for about 20 to 45 minutes. By using sintered CdTe source, the amount of CdTe consumed per deposition is kept to about 0.05 grams/micron.

The SnO₂/CdS coated 7059 glass substrate is loaded onto the transport system. The substrate is covered by a graphite cloth and then by a thin graphite plate on the top in order to provide uniform heating. The substrate temperature is read from the heaters placed just above the substrate.

The samples are annealed at 400°C in H₂ ambient for about 10 minutes to improve junction properties. This is done when the substrate is in position A, i.e. beneath heater H1.

After annealing, the chamber is evacuated and back filled with the desired amount of required gas. Generally CdTe is deposited in O₂, He or O₂ + He ambient. All the three heaters are turned on, and when all of them reach the required temperature the transport system moves to position B so that deposition takes place. The source and substrate temperature during deposition are in the range of 630°C – 690°C and 560°C-630°C respectively. After deposition the substrate is moved away from the source to position C.
and allowed to cool. The speed of the transport system, distance moved and the time of deposition are pre programmed and computer controlled.

3.4 Heating profile

A typical heating profile used for deposition is shown in figure 12. First, the substrate is under the annealing heater. After annealing the samples at 400 \(^\circ\)C in H\(_2\), the chamber is evacuated of H\(_2\), and back filled with O\(_2\), He, or He/O\(_2\) mixture. Heating profile is very important in determining not only the microstructure and growth, but also the junction properties. The substrate should not reach the required temperature much earlier than the source, as this may cause some of the CdS to vaporize depending on the total pressure in the chamber. In the small area CSS process, the substrate was kept above the source during the entire process including the heating up period. However, in the moving transport technique the samples are moved over the source only during the time of deposition.

Due to its larger mass, the source heats up at a slower. Therefore the source was turned on first. At a certain source temperature, the substrate heaters H1 and H2 are turned on. The heater H1, which is just above the substrate ramps at a slower rate. The condition established is such that, the heater H2 reaches the required temperature first. With in a few seconds the source reaches the deposition temperature. Immediately after all the three heaters reach the deposition temperature, the substrate is moved over the source to initiate the deposition process. After deposition, the substrate is moved away from the source and chamber is back filled with He. This will reduce the material consumption per deposition. In order to obtain reasonable and well defined temperature
profiles, it was necessary to perform a large number of calibration runs. Optimum set of control parameters were then selected.

Figure 12. Heating profile
Chapter Four

Results and Discussion

This chapter discusses the characterization of the large area CSS system for optimum deposition conditions. The effect of processing conditions on the film properties and device performance is discussed. Various measurement techniques namely current-voltage (J-V), spectral response (SR), capacitance measurements (C-V, C-F), and monochromatic light J-V measurement are briefly described.

4.1 J-V measurement

The J-V measurements determine the electrical characteristics of the device. The various device parameters like $V_{OC}$, FF, $J_{SC}$, $P_{max}$ and $\eta$ can be determined as explained in chapter one. The experimental setup consists of a simple solar simulator and a source meter coupled to a computer. The solar simulator is adjusted to AM 1.5 setting. A labview program runs the source meter which is used to sweep the voltage across the device. There is provision for separate voltage and current channels thereby reducing measurement errors. The measured currents are logged. The program also calculates the various device parameters and the characteristic curves are plotted.

4.2 Spectral response

The spectral response measurements involve the measurement of the photocurrent produced by light for a given wavelength and power. A tungsten light source is used. The
measurement is carried out at short circuit conditions. Light from the source passes through the gratings, and finally a spot light is focused on the sample by the use of optics. The light is narrowed by a slit arrangement in the monochromator. Current is measured from the sample as function of wavelength. The system is computer controlled. Pre-calibrated Si detectors are used for calibrating the light source.

4.3 Capacitance measurements

Capacitance measurements are carried out using a HP 4194A impedance/gain-phase amplifier. These techniques are used to study the movement of electronic charge with the device. The measurements are carried out in the dark. The capacitance voltage (C-V) measurement uses modulating voltage to determine the doping density of the device.

As there is a dependency of capacitance on frequency, the operating frequency was chosen such that stray capacitance is avoided. The frequency was kept at $10^6$ Hz. The oscillating voltage was 10 mV. The sweep range was from -2.0 V to 1 V. The capacitance frequency (C-F) measurement is used to identify traps that may exist in the device. The frequency was varied from 100 Hz to $10^6$ Hz.

4.4 Color J-V measurements

Wavelength specific J-V measurements provide valuable information about the collection related problems in solar cells. The measurement is carried out in a “black box” which is shielded from stray light and painted black on the interior. An EHP lamp is used as the light source. Different wavelengths can be chosen by using various band pass
filters having a band width of 20 nm. The filters are arranged in order on a rotating disc. The disc is motor driven which in turn is connected to a computer. A linearly graded intensity filter is used to adjust the intensity of light. The light from the source passes through the intensity filter and then through the wavelength filter and falls in the device. Proper shielding is provided to eliminate all stray white light. The intensity filter is also coupled to a computer controlled motor. Rotating the intensity filter varies the intensity. The AM 1.5 ISC of the device for bandwidth of different wavelengths are determined from spectral response measurements. The intensity of light is adjusted for this $I_{SC}$. The intensity can be varied to simulate different AM conditions.

### 4.5 Characterization of large area CSS system

The system can be segmented into two sub modules – the heaters and the transport system. These two sub modules require pre-deposition characterization. An assembly of three heaters are thermally shielded from each other and insulated with highly reflective molybdenum foils on the back side. The heaters are controlled by three Eurotherm 2208E temperature controllers. By tuning these heaters for required temperatures with minimum rise time, negligible overshoot and a small settling time is required. Preliminary tuning of the controllers, both separately and simultaneously was performed. Heat transfer due to radiation, convection and conduction may necessitate the need for sufficient correction to the estimated values of Proportional Band (PB), Integral Time ($T_i$) and Derivative Time ($T_d$). These values depend on the heat transfer properties of the system. The source heater reads the temperature from the graphite boat containing the source. The control parameters depend on the pressure in the vacuum system, the
weight of the graphite boat, and the order of tuning adopted. The order of tuning is the sequence and combination in which the controllers are tuned. Approximate values of the parameters are obtained by simulating the tuning cycle with thin graphite plates instead of the CdTe source. The sum of the weights of the graphite plates is approximately equal the weight of the CdTe used for making the source. The heaters are manually tuned for different weights of the graphite plate and the errors in the values of the parameters are reduced using an iterative method.

The annealing heater was tuned for both annealing and deposition conditions. The rise time of the two substrate heaters H1 and H2 are tuned such that the all three heaters reach the deposition temperatures at almost the same time. Typical values of the control parameters for 0.5 Torr pressure is shown in table 2

Table 2. Control parameters for heating assembly at 0.5 torr O2 pressure

<table>
<thead>
<tr>
<th>Control Parameters</th>
<th>Heater</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H1</td>
<td>H2</td>
<td>H3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Annealing</td>
<td>Deposition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PB</td>
<td>38.5</td>
<td>50.1</td>
<td>40.5</td>
<td>90.2</td>
</tr>
<tr>
<td>Ti</td>
<td>28</td>
<td>68</td>
<td>84</td>
<td>430</td>
</tr>
<tr>
<td>Td</td>
<td>4</td>
<td>11</td>
<td>14</td>
<td>71</td>
</tr>
</tbody>
</table>

The above parameters will provide a heating profile as shown in chapter 3. The fluctuations in temperature during deposition can be kept as low as 2°C at temperatures of around 650°C.
The transport system is another important module that has to be precisely controlled. The motion of the transport system is aided by a stepper motor, which is controlled by a Velmex VP9000 controller. The controller has a proficiency to operate either in the manual mode (Jog/Slew mode) or the computer mode (RS-232 mode). The controller can be programmed through the RS-232 port to control the speed, direction and distance of motion of the transport system. The motion can be accurate to 0.01 cm and the time/pause can be accurate to as much as to 1 ms. the controller was programmed through hyperterminal programming for the initial studies of the system. Upon optimizing the deposition conditions, the system can be programmed through a more sophisticated tool for complete automation.

Having tuned the temperature controllers and the Velmex controller, the system was then studied for optimizing it with minimum material consumption, high deposition rate and maximum device performance.

4.6 Initial calibration

Initial calibration was done by evaluating various deposition conditions using the stationary technique for deposition where in the substrate remains on top of the source throughout the entire time of processing including the time of ramping and annealing time. Hence the annealing heater and the transport mechanism are kept off. Approximate deposition conditions were first established. This technique is based on the small area CSS technique. The key factor was to simulate a deposition technique that could combine the best features of the CSS technique with advantages of moving transport technology.
Upon identifying the approximate parameters, moving substrate technology was studied. Various transport options were studied. First the deposition time was controlled by varying the speed of substrate transport. The speed of the transport system was controlled such that the substrate accelerates from the annealing zone and when it reaches the nearest edge of the source, moves at speed such that the time of exposure of the substrate to the source is controlled. Once the substrate moves out of the deposition zone, it accelerates away from the source. This technique was evaluated for various conditions and it was found that the films suffered from issues of nonuniformity and surface defects. In order to study and improve the uniformity of the films, the moving transport technique was modified for bidirectional movement. Here the deposition was carried out in two steps. The substrate accelerates to the source moves slowly over the source, first in the forward direction and upon reaching the farther end of the source changes direction and returns to the original position. Although the deposition had better uniformity than the unidirectional technique, the deposition tends to be more like a bilayer. Under high temperature conditions, there were issues of peeling and poor adhesion.

Both the above techniques suffered from more fluctuations in the substrate temperature during deposition than the conventional technique. Moreover, for the films made under identical conditions, the moving transport films were thinner than that obtained from the stationary process. The devices fabricated from the stationary technique had better performance than the latter.
4.7 Optimized moving transport technology

An optimum transport mechanism that provides high deposition rate, less temperature fluctuations and high efficiency devices was established. The order of processing is first to anneal in the annealing zone, moved forward rapidly and pause over the source for deposition and then move out of the deposition zone quickly. Typically, 99.9999% pure CdTe chunks were used for deposition. However, the use of sintered source provided better film surfaces and device performance. The spacing was kept as small as possible (0.7 – 1 cm). The main advantage of this technique was that it has the flexibility of either depositing on one large substrate or on four small substrates. The small substrates were further processed into solar cells and studied for device performance. The spatial uniformity of the device parameters was also studied.

4.8 Effect of ambient

4.8.1 Film characteristics

Oxygen ambient is preferred for the deposition of CdTe by CSS as it increases the acceptor density in the absorber. Although it reduces the deposition rate, the presence of O\textsubscript{2} decreases the pinhole density.

To study the effect of oxygen, the deposition was carried out in various pressures of O\textsubscript{2} keeping the other parameters constant. The deposition rate decreased with increase in oxygen content. O\textsubscript{2} oxidizes the source thereby reducing the source flux. Figure 13 shows the effect of O\textsubscript{2} pressure on the deposition rate. The material consumed per deposition decreased with increasing pressure. The plot of the amount of material consumed per micron of deposition against the O\textsubscript{2} pressure is shown in figure 14. As the
Figures 13 and 14 indicate both the deposition rate and material consumed decreases rapidly and levels after a certain pressure.
Figure 15.a. SEM of CdTe grown at 0.5 torr $O_2$

Figure 15.b. SEM of CdTe grown at 2 torr $O_2$

Figure 15.c. SEM of CdTe grown at 4 torr $O_2$
To further investigate the effect of ambient pressure, SEM images were taken. The films deposited at 0.5 torr, 2 torr and 4 torr O₂ are shown in figure 15. Figure 15.a shows a CdTe film deposited at 0.5 torr O₂. As seen, the films have a relatively smaller packing density. Large voids were observed. This could be due the high deposition rate where the particles accelerate towards the substrate at a fast rate. Hence some of the particles are loosely bound to the film and some of them can fall off leaving voids in the film. The grain size was in the range of 0.8 – 2 µm. The 2 torr films as shown in figure 15.b had higher packing density than the 0.5 torr films. The films are closely packed and no visible voids were observed. Although the films were thinner, problems of pinholes were not observed. The grain size of these films was in the range of 0.3-1 µm. Thus the grain size of the films decreased with increasing pressure. But the 4 torr sample shown in figure 15.c had grain sizes of about 0.3 – 1.5 µm. Hence a definite trend in the grain size was not observed. However the 4 torr sample were much more closely packed than those at lower pressures.

Thus it can be observed that the packing density increased with increasing pressure. The films were more reflective at higher pressures, but this is due to the decrease in thickness with increase in pressure. The variation in grain size may be due to variation in thickness as well. Hence investigations of films of similar thickness were studied. The surface roughness was also reduced which is also an effect of thickness of the films.
4.8.2 Devices performance

The device performance improved with increasing O$_2$ pressure. As observed in figure 16, the FF not only showed higher values but also improved uniformity at higher O$_2$ pressures. Interestingly, although the film thickness decreased with increasing pressure, the shunting was lower at higher pressures. This is believed to be due the high packing density exhibited at higher O$_2$ pressures.

![Figure 16. FF vs various deposition pressures](image)

Figure 17 is a comparison of the light J-V characteristics of devices made under different O$_2$ pressure. As the figure shows, the shunting decreased with increase in pressure. Lower FF’s can be attributed to poor collection exhibited at lower O$_2$ pressures. The $V_{OC}$’s improved slightly with increase in O$_2$ pressure. However no appreciable improvement was observed in $J_{SC}$.  

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The optimum pressure was chosen such that it is not too small to consume a lot of source material and not too high as to reduce the deposition rate by a large extent. Based on the above discussion, it can be concluded that the devices obtained at higher $O_2$ pressure showed improved performance.

4.9 Effect of substrate temperature

4.9.1 Film characteristics

As the substrate temperature was varied, there was no significant change in the material consumed. However, the deposition rate increased with increase in substrate temperature. This is shown in figure 18.
Figure 18. Deposition rate vs substrate temperature

SEM micrographs shown in figures 19 a and b, revealed that the grain size decreased with increase in substrate temperature. The films deposited at 580 °C had grain sizes in the range of 1-2.5 µm while the films deposited at 620 °C had grain sizes in the range of 0.5-1.5 µm. The samples deposited under lower substrate temperature were more reflective. This is effect of smaller thicknesses. A better understanding could be obtained by comparing samples with similar thickness.

Figure 19.a. SEM of CdTe film grown at substrate temperature of 580 °C
4.9.2 Device performance

Devices made at various substrate temperatures had $V_{OC}$’s and $J_{SC}$’s in the region of 790-830mV and 18 – 21mA/cm$^2$ respectively. The FFs showed uniform improvement at higher substrate temperatures. At lower substrate temperatures, a lot of shunting was observed. The variation of FF series and shunt resistance is shown in figure 20. Most of them were related to a thickness effect and surface defects. The maximum FFs were observed at higher substrate temperatures. This is because the deposition rate increased with increase in substrate temperature as shown in figure 18 and hence the films deposited at higher temperature were thicker and the light shunting was reduced. The series resistance decreased with increasing substrate temperature. This is also one of the main reasons for the drop in FF. Collection losses was more predominant at lower temperatures. Figure 21 a and b show the shunt effect exhibited at lower substrate temperatures.
Figure 20. FF and shunt resistance vs various substrate temperatures

Figure 21. (a) & (b) Light J-V and dark J-V characteristics of devices at different substrate temperatures to indicate shunting
4.10 Effect of source temperature and thickness

Varying the source temperature and keeping the other parameters constant increased the deposition rate. The material consumed per deposition also increased slightly. With thicker films, pinholes and void defects reduced. This would increase the shunt resistance and hence the fill factors. Figure 22 shows the improvement in FFs and shunt resistance with increases in the film thickness. The thickness was varied by varying the source temperature keeping other parameters constant.

![Figure 22. Fill factor, shunt resistance vs thickness](image)

4.11 Best device

The best devices were fabricated at higher O₂ pressures and higher substrate temperature. The best device produced by this technology is shown in table 3.
Table 3. Best devices by moving transport technique

<table>
<thead>
<tr>
<th>Conditions</th>
<th>VOC (mV)</th>
<th>FF (%)</th>
<th>JSC (mA/cm²)</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td># 6-25-1</td>
<td>830</td>
<td>70.6</td>
<td>21.1</td>
<td>12.36</td>
</tr>
</tbody>
</table>

Table 4. Distribution of device parameters for the best deposition condition

<table>
<thead>
<tr>
<th>FF Distribution</th>
<th>VOC Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>A</td>
<td></td>
</tr>
<tr>
<td>71.5</td>
<td>820</td>
</tr>
<tr>
<td>70.7</td>
<td>820</td>
</tr>
<tr>
<td>71.9</td>
<td>820</td>
</tr>
<tr>
<td>B</td>
<td></td>
</tr>
<tr>
<td>72.9</td>
<td>820</td>
</tr>
<tr>
<td>72.1</td>
<td>820</td>
</tr>
<tr>
<td>72.3</td>
<td>820</td>
</tr>
<tr>
<td>C</td>
<td></td>
</tr>
<tr>
<td>73.5</td>
<td>820</td>
</tr>
<tr>
<td>73.3</td>
<td>820</td>
</tr>
<tr>
<td>74.2</td>
<td>820</td>
</tr>
<tr>
<td>B</td>
<td></td>
</tr>
<tr>
<td>73.5</td>
<td>820</td>
</tr>
<tr>
<td>74.8</td>
<td>820</td>
</tr>
<tr>
<td>74.9</td>
<td>820</td>
</tr>
<tr>
<td>D</td>
<td></td>
</tr>
<tr>
<td>820</td>
<td>810</td>
</tr>
<tr>
<td>820</td>
<td>810</td>
</tr>
<tr>
<td>820</td>
<td>810</td>
</tr>
</tbody>
</table>

Devices made by stationary technique had a better uniformity and device performance than the devices made by the moving technology. The nature of growth of the CdTe film may be the predominant factor that establishes this behavior. In the stationary technique, the films start growing at a temperature lower than the set source temperature. This gradual growth facilitates better junction properties than the sudden abrupt growth as established by the moving transport technology. Table 4 shows the distribution of the FF and \( V_{OC} \)’s of the cells made in one deposition run for best large
area devices produced by stationary process. The thickness of the CdTe was about 5µm.

The J_{SC}’s were slightly above 21mA/cm^2.

Figure 23. Light and dark JV of the best device

Figure 24. Spectral response of the best device
The J-V curves shown in figure 23 and the spectral response shown in figure 24 exhibit good spatial uniformity. The devices had good fill factors over 70% and Voc’s around 820mV. From the spectral response curves, there seems to be some loss in the blue region. The currents could be improved by reducing the CdS thickness. Further investigation of the stationary process is suggested as much could not be studied during the course of this work due to equipment related problems.

4.12 Monochromatic light J-V measurement

Wavelength specific J-V measurements were done for different wavelengths from 460 to 775nm. This measurement was done for different intensities of light. The measurement is carried out for AM1.5 setting. This is obtained by adjusting the intensity of the light. Then the intensity of light is adjusted to produce the same $I_{SC}$ for all wavelengths. Figure 25 shows the color J-V measurements for one sun intensity and figure 26 shows the color J-V measurement at intensities to produce same $J_{SC}$ for different wavelengths. Both the graphs show poor collection at higher wavelengths. The higher wavelength photons penetrate deep. The photo carriers that are generated deeper at not completely collected. The drop in FF can be due to the poor collection of these deeply generated carriers. This trend was observed for intensities of 3 to 1/8 suns. This is shown in figure 27 and 28. As observed in figure 29 and 30 the shunt resistance and series resistance did not show much deviation neither with wavelength nor with intensity, the FF was dependent only on the collection function $J_L(V)$
Figure 25. J–V characteristic for different wavelength and same Jsc

Figure 26. J–V characteristic for different wavelength at AM 1.5
Figure 27. FF vs wavelength at same intensity

Figure 28. FF vs wavelength at same $J_{SC}$

Figure 29. Shunt resistance vs intensity for different wavelengths

Figure 30. Series resistance vs wavelengths for different intensities
4.13 Localized defects

Evidence of non uniform distribution of FFs on the same substrate was observed. This was mainly due to pin holes and or some localized defects. To verify the presence of such effects, samples were cut into halves and remeasured. It was found that one of the halves had a poor performance while the other had good FF. Table 5 shows clearly that the poor FF was due to such local defect or pin holes.

Table 5. Table showing evidence of localized defects

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Before breaking</th>
<th>After breaking</th>
</tr>
</thead>
<tbody>
<tr>
<td># 5-22-B1-b</td>
<td>61.9</td>
<td>56</td>
</tr>
<tr>
<td># 5-22-D1-b</td>
<td>44.7</td>
<td>30.1</td>
</tr>
</tbody>
</table>

4.14 C-V measurement

If a uniform doping profile is assumed, a plot of $A^2/C^2$ vs $V$ will contain the doping concentration ($N_a$) in the slope and the built-in potential ($V_{bi}$) as the intercept. This plot should be a straight line. If curvature is observed then there could be a doping profile across the space charge region. A horizontal line in reverse bias indicates that the device is completely depleted. The doping concentration of the large area devices were found to be in the order of $10^{14}$ which is in good agreement with literature. Depletion width was calculated at zero bias. Figure 31 shows the depletion width measured for different processing conditions. The depletion width increased with the substrate
temperature. This is due to sulphur in CdTe modifying the depletion width. It can be due the effect of interface on the depletion width.

![Graph showing depletion widths for different samples](image)

**Figure 31. Depletion widths for different samples**

### 4.15 C-F measurement

The capacitance frequency measurement gives information about the existence of traps in the depletion region. There is a gradual drop in the measured capacitance value with increase in frequency. At low frequencies, charges have enough time to move in and out of these traps and contribute to higher capacitance. With a shorter lifetime at higher frequencies, these charges are frozen [22]. Most of the devices do not show any predominant trap at any specific frequency except the 0.5 torr sample deposited at lower substrate temperature. Figure 32 shows the C-F plots for different conditions. The
emission rate of these traps can be found in Figure 33. The point of inflection in the curve is \( \omega_0 \). The emission rate was found to be 3.2 E-4.

Figure 32. Capacitance- frequency plots under dark conditions

Figure 33. \(-f_dC/df\) versus F for determining \(\tau\)
4.16 Material utilization

Upon optimizing for bets deposition conditions, it was found that this system had more than 90% material utilization based on the calculation below.

Weight of CdTe used per deposition = 0.2 gm

Weight of CdTe deposited on the substrate = $6.2 \times 5 \times 10^{-4} \times 9 \times 2.54 \times 2.54 = 0.18$ gm

Weight of CdTe grams wasted = 0.02 gm

Weight of CdTe wasted per unit length= 6.56 E -4

If all the losses are across the perimeter, it can be concluded that scaling the device size would result in lesser material losses. However, if correct for the spacing is incorporated, it can be concluded that atleast 90% material utilization can be achieved.
Chapter Five

Conclusion

Close spaced sublimation on moving substrates were investigated and partially optimized as a high efficiency module where films with acceptable uniformity and reproducibility were achieved. This technology could pose a potential candidate for next generation thin film photovoltaic technology. With the high deposition rates achieved and the use of moving transport mechanism, the system has a potential to provide good equipment cycle time in addition to its high reliability, repeatability, source material utilization and good conversion efficiency.

The films were investigated for various substrate and source temperature, ambient pressure and spacing. The devices showed an improved performance upon increasing the oxygen content. However, the deposition rate and the material consumed decreased with increasing pressure. Devices made at higher substrate temperatures performed better. The spacing was reduced to the possible minimum to increase the deposition rate and material utilization.

The fill factors of some devices low. This is due to pin holes and point defect in the CdTe film. Most of them were thickness related and thinning of the film at the edges. Devices had better characteristics upon increasing the thickness to about 5 microns. The device had lower currents in the lower wavelength region. Most of the devices were made on slightly thicker CdS. Decreasing the CdS thickness will increase the current. Devices
made on thinner CdS have to be investigated as this could give better overall current densities.

Devices made by stationary technique had better performance than the moving transport technology indicating that further investigation and optimization of the time of transfer of substrate has to be conducted to understand the effect of the nature of film growth. Effect of time of transfer of the substrates on the device performance has to be investigated. Heating profiles also play an important role in determining the properties of films made. This has to be explored further. The best device had the following parameters: \( \eta = 12\% \), \( \text{Voc} = 830 \text{ mV} \), \( \text{FF} = 74\% \) and \( \text{Jsc} = 21 \text{ mA/cm}^2 \).

The process of optimization can benefit from a fully automated deposition system. This would enable a more efficient temperature control and could save the time consumed to manually tune the controllers for each condition.
References


