Cadmium Zinc Telluride Solar Cells by Close Spaced Sublimation

by

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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 University of South Florida

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Keywords: CZT, Thin films, Processing, TCO, Superstrate configuration

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DEDICATION

This thesis is dedicated to my family for their everlasting love and support.
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CADMIUM ZINC TELLURIDE SOLAR CELLS BY CLOSE SPACED SUBLIMATION

Madhan Raj Ramalingam

ABSTRACT

Cadmium Zinc Telluride (Cd₅Zn₄Te or CZT) is a ternary semiconductor with a tunable bandgap of 1.44-2.26 eV. Solar cells with efficiencies of 20% or higher can be achieved by using a tandem solar cell structure which consists of a top cell and a bottom cell connected in series. In this kind of a structure, the light passes through the top cell first which has a wider bandgap to absorb light of shorter wavelengths and the remaining light passes through the bottom cell with a lower bandgap to absorb light of higher wavelengths. For a tandem cell structure, the ideal bandgap for the top and bottom cell is 1.7 eV and 1 eV respectively. Cadmium Zinc Telluride is a suitable candidate for the top cell and Copper Indium Gallium Diselenide (CIGS) with a bandgap of around 1 eV is a suitable candidate for the bottom cell.

This work involves characterization and optimization of CZT solar cells by Close Spaced Sublimation (CSS). Cadmium Zinc Telluride is deposited by the co sublimation of Cadmium Telluride (CdTe) and Zinc Telluride (ZnTe) chunks. Cadmium Zinc Telluride solar cells were fabricated using Tin Oxide (SnO₂), Zinc Oxide (ZnO) and Zinc Stannate (Zn₂SnO₄) films as substrates. The as-deposited CZT films were studied by
XRD, EDS and SEM measurements. The devices were characterized by Current-Voltage (I-V) and Spectral Response measurements.
CHAPTER 1

INTRODUCTION

Human beings have constantly been on the lookout to utilize every source of energy available to assist them in their quest for inventing new technologies. In simple words, electric power is the backbone for any kind of technological revolution that has taken place in the past or is about to take place in the future.

1.1 Energy Sources

The various energy sources available can be categorized into two – non-renewable and renewable energy source. The non-renewable energy source mainly comprises of fossil fuels like coal, oil, natural gas and nuclear energy. With the availability of abundant and inexpensive fossil fuels, the world energy consumption has been increasing tremendously over the century due to an increase in the human population. Although fossil fuels and nuclear energy now meet about 95% of the world’s energy needs, each of these energy sources has its own drawbacks when compared to renewable energy source. The burning of fossil fuels produces a lot of air pollutants like carbon monoxide, nitrogen oxide, sulphur dioxide, etc that can prove to be very
detrimental to the human body when inhaled over the long run[1]. Nuclear energy on the other hand has created concerns about radioactive waste disposal.

The various forms of renewable energy sources are solar energy, hydroelectric energy, biomass energy, geothermal energy and wind energy. Out of all these energy sources, solar energy is considered to be limitless, cheap and non-polluting. Even at its distance of about 93 million miles, sun is the dominant source of energy for our planet. The sun can be described as a sphere of gas heated by a nuclear fusion reaction at its center[2]. This massive hot body in turn emits radiant energy called light which plays an important role for life on our planet.

1.2 Solar Cells

A solar cell is a simple p-n junction diode which converts solar energy to electrical energy when light is shone over it. A solar cell works on the principle of photovoltaic effect. When photons from the sunlight strike a solar cell, they may be absorbed, reflected or transmitted. The absorbed photons transfer their energy to the electrons present in the atom of the semiconductor. With this high energy, the electron escapes from its normal position and is free to move. This free electron corresponds to the current output from a solar cell. This effect of converting light energy to electrical energy is known as photovoltaic effect. Photovoltaic effect was first observed by Becquerel[3] in 1839 when he produced a current by exposing silver electrodes to radiation in an electrolyte.
1.2.1 Types of Solar Cells

The different types of solar cells are single crystalline and polycrystalline solar cells. Single crystalline and polycrystalline solar cells currently available in the market are mostly silicon solar cells. Single crystalline silicon solar cells are limited to about 25% efficiency because they are mostly sensitive to infrared light, and radiation in this region of the electromagnetic spectrum is relatively low in energy. Polycrystalline silicon solar cells are significantly cheaper to produce than single crystalline cells but their efficiencies are also limited to less than 20% due to the internal resistance present at the boundaries of the silicon crystals. Thin film solar cells, which are also polycrystalline, can be made on low cost substrates such as glass, polymer or plastic. The other advantages are that they have a simple manufacturing process with the ability to achieve quite high conversion efficiencies. There are several deposition techniques available for thin film manufacturing and a noteworthy point here is that all the processes are less expensive compared to the complicated and clean manufacturing procedures required for silicon solar cell manufacturing. Thin film semiconductor materials that have been investigated so far are group III-V and II-VI compounds. III-V compounds mainly comprise of Gallium Arsenide (GaAs) but haven’t gained much interest due to the high cost of production and environmental considerations, as arsenic is extremely hazardous. In the II-VI set of compounds, Cadmium Telluride (CdTe) and Copper Indium Diselenide (CIS) play a major role in thin film solar cells manufacturing. CdTe is one of the most promising absorbers (p-type film) for solar cell fabrication due to its high absorption co-efficient and a bandgap of 1.45 eV which is the ideal bandgap
required by a material to absorb most of the light from the sun. SnO₂/CdS/CdTe thin film solar cells manufactured by Metal Organic Chemical Vapor Deposition (MOCVD) SnO₂ as the Transparent Conducting Oxide (TCO), chemical bath deposited Cadmium Sulphide (CdS) as the n-type window layer and CdTe deposited by Close Spaced Sublimation (CSS) as the p-type absorber layer have recorded efficiencies of 15.8% [4] here at the Thin Film Semiconductors laboratory in University of South Florida. To provide a perspective on the potential of photovoltaics for converting sunlight to electricity, it is interesting to compare thermodynamic and predicted (calculated) limits of efficiency with present-day device performance. In Figure 1, the best single-junction cell results have been compared to the maximum-achievable efficiency for AMO and AM1.5 solar spectra.

Figure 1 Comparison of Solar Cell Efficiencies to Predicted Limits[5] and the black-body limit. Single-crystal solar cells have reached more than 90% of their ultimate performance, while the best thin-film devices have typically reached 55%-65% of their ultimate performance. For most thin-film technologies,
laboratory cells have demonstrated only about 75% of their potential based upon the best cell parameters like Open Circuit Voltage ($V_{oc}$), Short Circuit Current ($J_{sc}$) and Fill Factor (FF)[5].

1.3 Tandem Solar Cells

To achieve efficiencies greater than 20%, we need to have two p-n junctions in series with one placed on top of another. This type of a structure is called a tandem solar cell. For a tandem solar cell to have higher efficiencies, the top cell should have a higher bandgap (~1.7 eV) to absorb light at shorter wavelengths and transmit light at longer wavelength and the lower cell should have a lesser bandgap (~1.0 eV) to absorb light at longer wavelengths. One more important point to be noted in a tandem solar cell structure is that the top cell is responsible for almost two thirds of the final output. There are two types of tandem solar cell structures namely two terminal structure and four terminal structure. These structures have been explained in the following section.

1.3.1 Two Terminal Tandem Solar Cell Structure

In a two terminal tandem structure as shown in figure 2, both the bottom and the top cell are grown as a series of layers one over another with an ohmic interconnect or an encapsulant between the two cells that is highly conductive and transparent. The major problem faced in a two terminal structure is that the photocurrents generated from both the cells must match each other to achieve higher efficiencies. If this fails to happen, then the total current generated would be equal to the lowest current generated between the two cells.
1.3.2 Four Terminal Tandem Solar Cell Structure

In a four terminal tandem structure as shown in figure 3, the only difference is that each cell has its own independent terminals (p and n) unlike the two terminal structure. Another advantage of using a four terminal device is that the ranges of acceptable bandgaps that produce the higher efficiency are considerably broader i.e., a bottom cell with bandgap of 1.0 eV and a top cell with bandgap of 1.7 eV can give a combined efficiency of ~34 %[6].
1.4 Cadmium Zinc Telluride, Cd\(_{1-x}\)Zn\(_x\)Te (CZT) Solar Cells

Cadmium Zinc Telluride (CdZn\(_x\)Te\(_{1-x}\)) with a tunable bandgap of 1.44 – 2.26 eV is an ideal candidate for the top cell. This work focuses on the processing and optimization of CZT solar cells on different Transparent Conducting Oxides (TCO). Cadmium Zinc Telluride was deposited by CSS technique which by far is one of the cheapest methods of deposition to yield devices with higher efficiencies with no reliability and reproducibility issues[7]. Cadmium Zinc Telluride was deposited on various TCO layers like SnO\(_2\), ZnO and ZTO. The as deposited CZT film was subjected to various post deposition treatments before contacting. The CZT films were studied by XRD, SEM and EDS measurements to determine the crystal orientation and zinc composition in the films. Transmission measurements were done to determine the amount of light transmitted through the films and to also determine the bandgap of the films. Completely fabricated CZT solar cells were characterized by light and dark I-V and spectral response measurements.
CHAPTER 2

SEMICONDUCTOR THEORY AND SOLAR CELLS

2.1 Types of Solids

The energy of an electron in a crystal lattice must always lie within well defined bands. The band that is responsible for the formation of bonds between atoms is called the valence bond. The next higher band present is called the conduction band. The separation between the energies of the highest valence band and lowest conduction band is called the energy gap or band gap of the material. Based on the energy band structure, solids can be classified into three types.

2.1.1 Conductors

As the name suggests, conductors have very good electrical conductivity (~ $10^{22}$ carriers/cm$^3$). Metals like aluminum, copper, etc can be classified as conductors. In conductors, both the valence and the conduction bands are normally half-filled.

2.1.2 Insulators

Insulators have very low conductivity (few thousand carriers/cm$^3$) or in other words have very high resistance to current flow. In insulators, there are no electrons in the conduction band and the energy gap is also very large.
2.1.3 Semiconductors

Semiconductors have their conductivity lying between that of a conductor and an insulator (~ \(10^{10}\) carriers/cm\(^3\))[8]. Let’s discuss in detail about semiconductors in the following section.

2.2 Semiconductor Theory

A semiconductor in simple terms can be called as an insulator with a narrow forbidden bandgap. At low temperatures as shown in figure 4(a), there is no conduction as the valence electrons don’t have enough energy to break the bonds and move to the conduction band.

But at high temperatures as shown in figure 4(b), the electrons in the valence band get excited and hence move to the conduction band leaving behind a hole in the valence band. This attributes to the flow of current in the form of electrons in the conduction band and holes in the valence band. Another important term that needs to be understood at this point is the Fermi level. It is defined as an energy level that lies between the valence and
conduction band at such a point where there is 50% probability of being occupied by an electron[9].

\[
\begin{align*}
    f(E) &= \frac{1}{1 + e^{-\frac{E - E_f}{kT}}} \\
    \text{Where}, \\
    E_f &\text{ is the Fermi level} \\
    k &\text{ is the Boltzman constant} \\
    T &\text{ is absolute temperature in } ^{0}\text{K}
\end{align*}
\]

At thermal equilibrium, the number of electrons (n) in the conduction band and number of holes (p) in the valence band is given by,

Figure 5 Fermi Dirac Distribution

The probability of a state with energy \( E \) being occupied by an electron is given by the Fermi-Dirac distribution function \( f(E) \) (Figure 5) as follows:
\[
\begin{align*}
n &= N_c e^{-\frac{(E_c - E_f)}{kT}} , \\
p &= N_v e^{-\frac{(E_f - E_v)}{kT}}
\end{align*}
\]

Where,

\(n\) is the number of free electrons per cm\(^3\)

\(p\) is the number of holes per cm\(^3\)

\(N_c\) is the effective density of states in the conduction band per cm\(^3\)

\(N_v\) is the effective density of states in the valence band per cm\(^3\)

2.3 Types of Semiconductors

Semiconductors are mainly classified into two types – Intrinsic and Extrinsic. Before getting into detail about the types of semiconductors, let us discuss in brief about another important term called doping. Doping is the process of intentionally adding small amounts of impurity atoms to a pure semiconductor to make it conductive.

2.3.1 Intrinsic Semiconductor

Intrinsic semiconductors otherwise called as pure semiconductors contain atoms of the semiconductor alone without any external dopant atoms. Thus, for an intrinsic semiconductor, the fermi level would lie exactly at the middle of the band gap as shown in figure 6.

\(E_c\)  

\(E_f\)  

\(E_v\)

Figure 6 Intrinsic Semiconductor
2.3.2 Extrinsic Semiconductor

As the name suggests, in an extrinsic semiconductor, small amounts of impurity atoms are added to the pure semiconductor to make it conductive. Depending upon the type of dopant atoms added, extrinsic semiconductors can be classified as either n-type or p-type.

2.3.2.1 N-type Dopant

In the case of Si, n-type doping involves doping by a pentavalent impurity (Si is tetravalent) like P or As as shown in figure 7. The majority carriers in this type of doping are electrons. They are also called donor atoms as they donate a free electron to the semiconductor[10]. II-VI semiconductors like CdTe, CdS can be doped n-type by adding any group VII element to these semiconductors. In an

Figure 7 N-type Si with Phosphorous Impurity
n-type semiconductor, as there is a high concentration of electrons in the conduction band than the valence band, the fermi level lies closer to the conduction band as shown in figure 8.

\[ E_c \]
\[ E_F \]
\[ E_v \]

Figure 8 N-type Semiconductor

### 2.3.2.2 P-type Dopant

Similarly, in the case of Si, p-type doping involves doping by a trivalent impurity like B as shown in figure 9. The majority carriers in this type of doping are holes and they are also called acceptor atoms as they accept a free electron to the semiconductor.

Figure 9 P-type Si with Boron Impurity
II-VI semiconductors like CdTe, CdS can be doped p-type by adding any group I element to the semiconductor. In a p-type semiconductor, as there is a low concentration of electrons in the conduction band than the valence band, the fermi level lies closer to the valence band as shown in figure 10.

\[ E_c \]

\[ E_f \]

\[ E_v \]

Figure 10 P-type Semiconductor

### 2.4 P-N Junction

When a p-type and an n-type semiconductor material are joined together, the interface formed between them is called a p-n junction. Under equilibrium, electrons from the n-type material near the junction diffuse across the junction and fill the holes in the p-type material. This gives rise to diffusion current \( J_{\text{diff}} \). Donor ions are therefore created on the n-side of the junction as a result of electrons leaving the n-type material. Similarly acceptor ions are created on the p-side of the junction as a result of holes leaving the p-type material. As the electrons and holes meet at the junction, they recombine and no longer carry any charge[11]. This region that is depleted of any charge is called the space charge region or depletion region as shown in figure 11. Whenever there is a positive charge present with respect to a negative charge, a potential difference is set up between the charges[12]. This potential barrier that builds up blocks the carrier...
diffusion across the junction. As a result, the electrons from the p-side start drifting towards the n-side and vice-versa giving rise to drift current $J_{\text{drift}}$.

Figure 11 P-N Junction

The drift current is always opposite to the diffusion current under equilibrium ($J_{\text{diff}} + J_{\text{drift}} = 0$). Also at equilibrium, the fermi level must be constant throughout the junction. This results in the bending of the p-type and n-type conduction bands at the junction (Figure 12) which leads to the formation of a potential difference across the depletion region called as the built-in potential, $V_{\text{bi}}$. This potential difference, $V_{\text{bi}}$, acts as a barrier allowing the current to flow across the junction in only one direction i.e., making the junction to act as a rectifier.

Figure 12 Energy Band Diagram of P-N Junction
The built-in potential, $V_{bi}$ is given by the following equation.

$$V_{bi} = \frac{kT}{q} \ln \left( \frac{N_A N_D}{n_i^2} \right)$$

Where,

- $N_A$ is the acceptor impurity concentration per cm$^3$
- $N_D$ is the donor impurity concentration per cm$^3$
- $n_i$ is the intrinsic impurity concentration per cm$^3$

The total depletion width, $W$ is given by,

$$W = \left[ \frac{2\varepsilon}{q} \left( \frac{N_A + N_D}{N_A N_D} \right) (V_{bi} - V) \right]^{1/2}$$

Where,

- $V$ is the external voltage bias across the junction in volts
- $\varepsilon_s$ is the permittivity of the semiconductor

When a reverse bias is applied to a p-n junction, the barrier height increases and retards the flow of the majority carriers. Therefore in reverse bias, the minority carriers start to drift resulting in a very small drift current $J_{drift}$ and almost zero diffusion current $J_{diff}$.

When a forward bias is applied, the depletion width reduces which in turn reduces the built in field and the barrier height. This allows more majority carriers to flow across the junction, resulting in a larger current.

### 2.4.1 Types of P-N Junctions

#### 2.4.1.1 Homojunction

A p-n junction formed between the same semiconductor acting as the p-type and n-type material is known as homojunction. A junction formed between
p-type Si doped with boron and n-type Si doped with phosphorus is an example of homojunction.

**2.4.1.2 Heterojunction**

The junction formed when two different semiconductors doped p-type and n-type are brought together is called a heterojunction. The energy band diagram prior to the junction formation is shown in figure 13.

![Energy Band Diagram before Junction Formation](image)

Before analyzing the band structure, let us discuss about a few important terminologies that we will use in the course of the explanation. Electron affinity, $\chi$ is the energy required to remove an electron from the bottom of the conduction band, $E_c$. The energy required to remove an electron from the fermi level, $E_f$ is called the work function, $\Phi_m$. The two materials in fig 8 have different bandgaps $E_{g1}$ and $E_{g2}$, different electron affinities $\chi_1$ and $\chi_2$, different work functions $\Phi_1$ and $\Phi_2$ and different permittivities $\varepsilon_1$ and $\varepsilon_2[13]$. The energy band diagram at equilibrium after forming the heterojunction is shown in figure 14. The
discontinuities in the conduction and valence bands can be represented by the following equations,

\[ \Delta E_c = \chi_1 - \chi_2 \]
\[ \Delta E_v = (E_{g2} - E_{g1} - \Delta E_c) \]

This discontinuity is caused due to the difference in bandgaps, electron affinities and work functions of the two materials. Also a point to be noted here is that due to the small \( \Delta E_c \), the minority carriers in the p-side will not be impeded from flowing across the junction but the discontinuity in the valence band, \( \Delta E_v \) forms a barrier for the flow of minority carriers (holes) from the n-side to the p-side.

![Figure 14 Energy Band Diagram after Junction Formation](image)

2.5 Solar Cells

A solar cell is a p-n junction diode which works on the principle of photovoltaic effect i.e., by converting sunlight directly into electricity when the light is shone on the solar cell. The sun is the only natural source of light for the earth that radiates an essentially continuous black body spectrum of electromagnetic radiation at 6000 K.
(Figure 15). A quantity called air mass or solar constant is normally used to quantify the amount of energy received on the earth’s surface. Air mass is defined as the degree to which the atmosphere affects the sunlight received at the earth’s surface. The atmosphere effect is mainly attributed to attenuation of sunlight due to water vapor absorption, ozone absorption and scattering by airborne dust particles. The secant of the angle between the sun and the zenith (sec θ) is called the air mass and it measures the atmospheric path length relative to the minimum path length when the sun is directly overhead[9]. Air mass 1.5 (sun at 45° above the horizon) has been proven to be the optimum value for terrestrial applications.

2.5.1 Solar Cell Working

When light (photons) is incident on a semiconductor surface, part of it is reflected and the rest is transmitted or absorbed. A photon with energy less than the bandgap of the semiconductor does not contribute to the photovoltaic effect. A photon with energy greater than the bandgap is absorbed by the semiconductor
and in turn leads to the formation of Electron-Hole Pairs (EHP) by optical excitation and the excess energy generated is released as heat[15]. These electron-hole pairs are separated across the junction leading to the generation of current. The amount of light that is transmitted by the semiconductor is given by the following equation.

$$I_t = I_0e^{-\alpha t}$$

Where,

- $I_t$ is the light in the semiconductor at depth $t$ from the surface
- $I_0$ is the intensity of light incident on the semiconductor
- $\alpha$ is the absorption co-efficient of the semiconductor
- $t$ is the depth of the semiconductor material from the surface of incident light

The energy of the incident light can be obtained by the relation,

$$E = h\nu = \frac{hc}{\lambda} = \frac{1.24}{\lambda} \text{ eV}$$

Where,

- $h$ is the Planck’s constant
- $c$ is the velocity of light ($3 \times 10^8$ m/sec)
- $\lambda$ is the wavelength of light

### 2.5.2 Solar Cell Parameters

The current-voltage characteristics (I-V) under dark and light conditions is shown in figure 16. The I-V curve is obtained by plotting the output current as a
function of the voltage. The total current flowing through a circuit in the presence of light is given by,

\[ I = I_o \left[ e^{\frac{qV}{Akt}} - 1 \right] - I_L \]

Where,

- \( I_0 \) is the reverse saturation current
- \( A \) is the diode quality factor
- \( I_L \) is the light generated current

![Figure 16 Dark and Light I-V Curves](image)

Now, let us discuss about some of the parameters that play an important role in the performance of a solar cell.
2.5.2.1 Short Circuit Current, $I_{sc}$

As the name suggests, it is the current obtained when the solar cell is short circuited or in other words when there is no voltage applied to the cell. Hence the current equation reduces to

$$I_{sc} = -I_L$$

i.e., the short circuit current is the same as the light generated current, $I_L$. Short circuit current is normally represented as current density, $J_{sc}$ (mA/cm$^2$) which is given by

$$J_{sc} = \frac{I_{sc}}{A}$$

Where,

$A$ is the area of the solar cell

2.5.2.2 Open Circuit Voltage, $V_{oc}$

Open circuit voltage is the voltage obtained when the current is zero. In other words, it is the voltage obtained at the solar cell terminals when an infinite load is attached to it.

Open circuit voltage, $V_{oc}$ (mV) is given by the relation,

$$V_{oc} = A \left[ \frac{kT}{q} \right] \ln \left( \frac{I_{sc}}{I_o} + 1 \right)$$

2.5.2.3 Fill Factor, FF

From fig.16, we can see that $V_m$ and $I_m$ are the maximum voltage and current that can be achieved and the corresponding power $P_m$ is given by,

$$P_m = V_m I_m$$
This point \( P_m \) is located where the rectangle having the largest area can be drawn inside the I-V curve. The ratio of the peak output \((V_mI_m)\) to the variable output \((V_{oc}I_{sc})\) is called the fill factor, FF (%) of the solar cell and is given by,

\[
FF = \frac{V_mI_m}{V_{oc}I_{sc}}
\]

### 2.5.2.4 Efficiency, \( \eta \)

The efficiency of a solar cell is defined as the ratio of the photovoltaically generated output to the incident power falling on it. It is a measure of the light energy successfully converted to the electrical energy. Efficiency, \( \eta \) (%) is given by the relation,

\[
\eta = \frac{P_{out}}{P_{in}}
\]

\[
\eta = \frac{FF \times V_{oc} \times I_{sc}}{P_{in}} \times 100\%
\]

As the total radiated power incident on the cell \( P_{in} \) is 100, the efficiency reduces to

\[
\eta = V_{oc} J_{sc} FF
\]

### 2.5.3 Equivalent Circuit of a Solar Cell

The equivalent circuit of an ideal solar cell is shown in figure 17. However, when talking about real solar cells, the effect of series and shunt resistances should be taken into account as these parameters are dependant on the material properties and process technology.
2.5.3.1 Series Resistance, $R_s$

The major part of the series resistance mainly arises from the contact resistance of the front and back contacts of the solar cell. Some of the other components include the contact resistance between the metal and semiconductor and the ohmic resistance in the semiconductor material. Typical values of $R_s$ are 5, 10 and 15 $\Omega$. Higher $R_s$ values lead to a decrease in the FF of the solar cell which in turn affects the efficiency. The effect of $R_s$ on a solar cell performance is shown in figure 18.

![Figure 18 Effect of $R_s$ on Solar Cell Performance](image_url)
2.5.3.2 Shunt Resistance, $R_{sh}$

Shunt resistance mainly arises due to leakage current created within the solar cell. Some of the reasons for the occurrence of these leakage paths are due to recombination current, surface leakage and surface defects in the semiconductor. These leakage paths are not uniformly distributed and vary from one cell to another. The combined effect of all the leakage paths constitute the term called shunt resistance, $R_{sh}$ (figure 19). Typical values of $R_{sh}$ are $10^3$ to $10^7$ Ω.

![Figure 19 Effect of $R_{sh}$ on Solar Cell Performance](image)

2.5.3.3 Diode Quality Factor, $A$

The diode quality factor is used to determine the perfectness of the junction and it varies for every diode. It is due to physical phenomena such as surface effect, recombination and tunneling. It is a measure of how close the measured I-V characteristics match the ideal characteristics. For an ideal diode, diode quality factor is normally 1. High values of diode quality factor can lead to excess forward voltage, heating and a loss in the efficiency. Taking into effect the role of $R_s$ and $R_{sh}$, the equivalent circuit of a solar cell is as shown in figure 20.
Similarly, incorporating the effects of $R_s$, $R_{sh}$ and $A$, the total current flowing through the circuit is given by,

$$I = I_L + I_0 \left[ \exp \left( \frac{q(v - IR_s)}{AkT} \right) - 1 \right] + \frac{V - IR_s}{R_{sh}}$$

Where,

$I$ is the output current

$I_L$ is the light generated current

$I_0$ is the diode saturation current

$R_s$ is the series resistance

$R_{sh}$ is the shunt resistance

$A$ is the diode quality factor
3.1 Tin Oxide (SnO$_2$)

Tin Oxide (SnO$_2$), being a highly transparent material is the most commonly chosen Transparent Conducting Oxide (TCO) when compared to other TCO’s like Zinc Oxide (ZnO), Indium Tin Oxide (ITO), Cadmium Stannate (Cd$_2$SnO$_4$), etc. This is due to the excellent optical and electrical properties of this material like high transmittance, high conductivity, low reflectance and low sheet resistance (depends on doping). CdTe/CdS solar cells with a record efficiency of 15.8 %\cite{4} have been fabricated with SnO$_2$ as the TCO layer. SnO$_2$ can also be used when high temperature processing of CdS and CdTe is to be followed, because of its stable nature even at high temperatures\cite{16}. SnO$_2$ films can be deposited by various methods like spray pyrolysis, APCVD, MOCVD, Sputtering, etc. SnO$_2$ is a wide bandgap semiconductor (3.49 eV) with a tetragonal rutile structure\cite{17} as shown in figure 21. Each tin atom is at the center of six oxygen atoms and each oxygen atom in turn is surrounded by three tin atoms. The oxygen vacancies present are responsible for the n-type conductivity of the SnO$_2$ film. The conductivity of the SnO$_2$ films can be further enhanced by appropriate doping. Fluorine has proven to be an
efficient dopant for SnO$_2$ because of the higher conductivity, optical transmission and infrared reflection that the fluorine doped SnO$_2$ (SnO$_2$:F) films possess\cite{18}.

![Figure 21 Tin Oxide (SnO$_2$) Structure\cite{17}](image)

3.1.1 Deposition Techniques for SnO$_2$ Films

Some of the deposition techniques that are being followed for SnO$_2$ film deposition have been discussed in this section.

3.1.1.1 Atmospheric Pressure Chemical Vapor Deposition

Atmospheric Pressure Chemical Vapor Deposition (APCVD) technique is very widely used for SnO$_2$ deposition since it offers good control over the equipment and film properties, can employ lower growth temperatures, and can be used to deposit large area films continually. A conveyor furnace maintained at atmospheric pressure was used for the deposition of the SnO$_2$:F films. A constant temperature zone of 300-1200$^\circ$C was maintained in the middle of the furnace where the deposition normally takes place. SnCl$_4$ was used as the source for tin and oxygen and fluorine (C$_2$H$_4$F$_2$) were introduced into the chamber as reaction gas and dopant.
High purity N₂ was used as the carrier gas[19]. Figure 22 shows the XRD pattern of the SnO₂ films deposited by APCVD at various substrate temperatures, Tₛ. Curves a to d correspond to the XRD pattern of SnO₂:F films deposited at increasing Tₛ and curve e corresponds to the XRD pattern of undoped SnO₂ film deposited at the same temperature as c.

Figure 22 XRD Pattern of SnO₂ Films by APCVD[5]. Curves a to d = Doped samples, Curve e = undoped sample. Curve a: Tₛ = 400°C, Curve b: Tₛ = 450°C, Curve c: Tₛ = 500°C, Curve d: Tₛ = 550°C, Curve e: Tₛ = 500°C[19].

The XRD patterns show that SnO₂:F films deposited at Tₛ>400°C were polycrystalline. Also, the preferred crystalline growth orientations of these films varied with Tₛ. When Tₛ<450°C, films with (110) orientation were obtained, but when Tₛ>450°C, films with (200) orientation were obtained. It was also found that fluorine doping affected the preferred orientation of the films, i.e., when the Tₛ was 500°C, the preferred orientation was along the (200) plane whereas the preferred orientation for the undoped films at the same Tₛ was along the (211)
plane. The average total transmittance and diffuse transmittance spectra for these films were over 90% and 14%[19] as shown in figure 23.

![Figure 23 Transmission of SnO$_2$ Films by APCVD][5]. Films a, b, c = Total Transmittance, Films d, e, f = Diffused Transmittance. Curves a and d: SnO$_2$:F films; T$_s$ = 550°C, Curves b and e: SnO$_2$:F films; T$_s$ = 450°C, Curves c and f: SnO$_2$ films; T$_s$ = 400°C[19].

The SnO$_2$:F films deposited by APCVD also had very low resistivities of around 5 x 10$^{-4}$ Ωcm.

### 3.1.1.2 Spray Pyrolysis Technique

Spray pyrolysis technique is a simple and scaleable process and has been adopted to deposit high quality SnO$_2$:F films. An organometallic tin compound namely Dimethyl Tin Chloride ((CH$_3$)$_2$SnCl$_2$) was used as the tin source and HF + NH$_4$F compounds were used as the fluorine doping agents for the SnO$_2$ films[20]. The compound to be deposited was heated to about 500-530°C and the vapor generated was transported using air or oxygen as the carrier gas and was then
sprayed on to the substrates[20]. Figure 24 shows the XRD spectra of SnO$_2$:F films deposited at 450-500$^\circ$C having preferential (110) orientation.

![XRD spectra of SnO$_2$:F films](image)

Figure 24 XRD of SnO$_2$:F Films by Spray Pyrolysis Technique[20]

![Transmission spectrum](image)

Figure 25 Transmission of SnO$_2$:F Films by Spray Pyrolysis Technique[20]

SnO$_2$:F films deposited by this technique had transmittance of around 85% as shown in figure 25 in the visible region and resistivities of $4.1 \times 10^{-4}$ $\Omega$cm.
3.2 Zinc Oxide (ZnO)

Zinc Oxide (ZnO) film with a large bandgap of about 3.3 eV is one of the most potential materials for being used as a TCO because of it’s good electrical and optical properties, abundance in nature, absence of toxicity[21,22] and the ability to deposit these films at relatively low temperatures[23]. The oxygen vacancies and/or zinc interstitials correspond to the n-type conductivity of the ZnO films. The resistivity of these films can be further lowered by doping them with group III elements like B, Al, Ga or In. Among all these elements, Al is considered to be a good dopant for opto-electronic applications like solar cells due to the high transmittance that Al-doped ZnO films exhibit. ZnO has a hexagonal wurtzite structure as shown in figure 26 with the divalent cation (Zinc) in tetrahedral coordination with oxygen, and each oxygen in tetrahedral coordination with four divalent cations (zinc)[24].

![ZnO Crystal Structure](image)

Figure 26 ZnO Crystal Structure[24]

ZnO films can be deposited by various methods like sputtering, MOCVD[25], spray pyrolysis[26], pulsed laser deposition[27] and sol-gel method[28]. Among all these
techniques, sputtering is the most widely used deposition technique due to better adhesion of the deposit, higher density of films and the ability to work at low deposition temperatures. The sputtering targets used in the experiment were high purity ZnO (99.99%) and Al(OH)₃ (99.99%) powders[22]. Six targets (pure ZnO, 2, 4, 6, 8 and 10 wt.% of Al(OH)₃ doped ZnO) were prepared to study the properties of films deposited by each target. The base pressure in the chamber was ~ 3 x 10⁻⁶ Torr and the working pressure was 32 mTorr with high purity (99.99%) Ar as the sputtering ambient. The substrate to target distance (Dₛₜ) was varied from 35-80 mm, the substrate temperature (Tₛ) was varied from room temperature to 250°C and a RF power of 150 watts was used. Figure 27 shows the high resolution XRD pattern obtained for Al-doped ZnO films of varying thicknesses (75-2330 nm) with (002) preferred orientation in all the films.

![Figure 27 XRD of Al-doped ZnO Films of Varying Thicknesses][22]
Figure 28 shows the resistivity being affected due to (a) $D_{ts}$, (b) Al(OH)$_3$ content in the target and (c) substrate temperature, $T_s$.

![Figure 28 Resistivity of Al-doped ZnO Films[22] as a Function of (a) $D_{ts}$ (b) Al(OH)$_3$ Content in Target (c) $T_s$](image)

We can see from figure 28(a) that the resistivity remains nearly constant when $D_{ts} \leq 50$ mm. A similar effect is seen in figure 28(b) with respect to the Al(OH)$_3$ content in the target below and above 6wt.% of Al(OH)$_3$. The reason for the very low resistivities of Al-doped ZnO films prepared with less than 6%wt.% Al(OH)$_3$ doped ZnO might be due to the Al doping concentration, oxygen vacancies, Al and Zn concentrations at the interstitial sites, grain boundaries and ionized impurity scattering[29]. Figure 28(c) shows the effect of Al(OH)$_3$ content in the target below and above 6wt.% of Al(OH)$_3$ at $T_s = 250^\circ C$. Figure 29 shows the transmittance of Al-doped ZnO films under different conditions. From figures 29(a) and 29(b), it is evident that the transmittance decreases as the deposition time increases and $D_{ts}$ decreases. The decrease in transmittance due to
increase in thickness was due to the thickness effect, which lead to a decrease in light scattering losses[22].

Figure 29 Transmittance of Al-doped ZnO Films[22] with (a) Thickness (b) $D_{ts}$ (c) Al(OH)$_3$ content in target (d) Plot showing the optical bandgap for different Zn concentrations

The effect of bandgap ($E_g$) with increase in Al(OH)$_3$ content in the target is shown in figure 29(d) which shows that as the Al(OH)$_3$ content increases, the absorption edge shifts to the shorter wavelength region. In other words, $E_g$ widens with increase in Al content.
3.3 Zinc Stannate (Zn$_2$SnO$_4$)

Zinc Stannate, Zn$_2$SnO$_4$ (ZTO) is a highly transparent and highly conducting TCO which may be used as a suitable replacement for Cd$_2$SnO$_4$ (CTO) which has a relatively lesser conductivity[30]. ZTO is also used a high resistive buffer layer in CdTe/CdS solar cells resulting in higher currents. ZTO has an inverse cubic spinel structure as shown in figure 30.

![AB$_2$O$_4$ spinel](image)

A spinel structure can be divided into two types namely normal and inverse spinel structure. In normal spinel structure, the A cations occupy the tetrahedral sites and the B cations occupy the octahedral sites. The usual notation for this type of occupancy is (A)[B$_2$]O$_4$, where ( ) represents the tetrahedral sites and [ ] represents the octahedral sites.
Sometimes the A cations switch places with one half of the B cations, resulting in a structure known as the inverse spinel structure which is given by the notation (B)[AB]O₄. In some spinel structures, partial inversion takes place and this can be denoted by a parameter x, known as the degree of inversion[30]. This can be better understood by the formula (A₁₋ₓBₓ) [AₓB₂₋ₓ] O₄. Here, if x equals zero, it is a normal spinel structure, and if x equals one, it is an inverse spinel structure.

The ZTO films were deposited by RF magnetron sputtering using a ZTO target. The chamber was pumped down to a base pressure of 3 x 10⁻⁶ to 2 x 10⁻⁷ Torr and was backfilled with ultra high purity (99.993%) oxygen or argon to about 20mTorr. The films were deposited at 550-650°C at 250 watts RF power[30]. Post deposition anneals in Ar at 600°C were done to increase the crystallinity (amorphous to crystalline) and conductivity of the ZTO films. The XRD patterns of the as deposited or amorphous ZTO and annealed ZTO films is as shown in figure 31[31].

Figure 31 XRD of RF Sputtered ZTO Films[31]
3.4 Cadmium Zinc Telluride (Cd$_{1-x}$Zn$_x$Te)

Cadmium Zinc Telluride, Cd$_{1-x}$Zn$_x$Te (CZT), an alloy of Cadmium Telluride (CdTe) and Zinc Telluride (ZnTe) is a ternary compound with a tunable bandgap from 1.4 – 2.26 eV[32,33], which makes it a suitable candidate in the field of optoelectronic devices. CZT can also be used in gamma ray detectors and electro-optical modulators[34]. One of the most important applications of CZT film is its use as the top cell absorber material in a tandem solar cell structure due to its high bandgap[35]. Using a tandem solar cell structure, we can achieve cell efficiencies of greater than 20%. In a tandem solar cell structure, a high bandgap material is used as the absorber for the top cell and a low bandgap material is used as the absorber for the bottom cell. CIS and its alloys have been reported to be very good candidates for the bottom cell with efficiencies of 16-18%[36]. CZT and Cadmium Selenide (CdSe) are suitable choices for the top cell because of their high bandgap.

Top cells with CZT as the absorber layer have yielded efficiencies of ~7%[37]. CZT can be deposited by evaporation, sputtering, closed spaced sublimation, etc. CZT crystallizes in a zinc blende structure as shown in figure 32, similar to both CdTe and ZnTe. The transition from CdTe (x = 0) to ZnTe (x = 1) in Cd$_{1-x}$Zn$_x$Te occurs in a single
The concentration of zinc (x) in Cd$_{1-x}$Zn$_x$Te is governed by Vegard’s law, which states that the lattice parameter has a linear relationship with the zinc concentration. In CZT films, the lattice parameter decreases (Table 1) with the increase in the zinc concentration as shown in figure 33.

Table 1 Lattice Constants for Different Zn Concentrations

<table>
<thead>
<tr>
<th>Cd$_{1-x}$Zn$_x$Te</th>
<th>Lattice Constant(A°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdTe(x=0)</td>
<td>6.481</td>
</tr>
<tr>
<td>Cd$<em>{0.95}$Zn$</em>{0.05}$Te</td>
<td>6.465</td>
</tr>
<tr>
<td>Cd$<em>{0.70}$Zn$</em>{0.30}$Te</td>
<td>6.364</td>
</tr>
<tr>
<td>Cd$<em>{0.50}$Zn$</em>{0.50}$Te</td>
<td>6.287</td>
</tr>
<tr>
<td>ZnTe(x=1)</td>
<td>6.102</td>
</tr>
</tbody>
</table>
By curve fitting the points in figure 33, we get the equation for finding the concentration of zinc \((x)\) as follows,

\[
a = 6.481 - 0.3837(x)
\]

Where,

\(a = \text{Lattice constant (found from XRD data)}\)

In the evaporation process discussed here, two different sources (CdTe and ZnTe) were co-evaporated[32] to form CZT films. 5N pure CdTe and ZnTe compounds, used as the evaporation sources were put into two separate crucibles. The two sources were positioned in such a way so that the substrates placed above were uniformly exposed to both the sources during deposition. The substrates were kept at 573 K and the chamber was pumped down to a base pressure of \(5 \times 10^{-6}\) Torr. The deposition rate of CdTe was
kept at 20 Å/sec whereas the deposition rate of ZnTe was varied to obtain Cd$_{1-x}$Zn$_x$Te films of different Zn(x) compositions. The XRD of the films are as shown in figure 34.

![Figure 34 XRD of Cd$_{1-x}$Zn$_x$Te Films][32]

The XRD pattern revealed that the films were polycrystalline in nature with preferred (111) orientation which represents a cubic structure. There were no diffraction peaks associated with CdTe and ZnTe, which indicated that the CZT films were of single phase. The optical transmission of CZT films for varying x values is shown in figure 35.

![Figure 35 Transmission of Cd$_{1-x}$Zn$_x$Te Films][32]
High transmission in the longer wavelength region was observed and the absorption edge was found to shift towards the shorter wavelengths as the Zn content in the films increased.

![Figure 36 Bandgap of Cd$_{1-x}$Zn$_x$Te Films][32]

The bandgap ($E_g$) of the CZT films with varying Zn concentration was estimated by calculating $(\alpha h \nu)^2$ and plotting it against $h \nu$ as shown in figure 36.
CHAPTER 4

SOLAR CELL PROCESSING

4.1 Device Structure

The device structure used in this research work is the superstrate configuration shown in figure 37.

![Figure 37 CZT Cell Structure](image)

The substrate used in this study was 7059 Corning glass. This glass substrate measures 3.5x3.5 cm² and is 1mm thick. It is highly transparent with a transmittance of nearly 100%. This work focussed on CZT solar cells fabricated on various transparent conducting oxides. The different TCO’s used were Tin Oxide (SnO₂), Zinc Oxide (ZnO) and Zinc Stannate (Zn₂SnO₄). The absorber layer used in this work was CZT which was deposited by Close Spaced Sublimation (CSS) process. Graphite paste doped with HgTe:Cu was used as the back contact for the CZT cell structures that were fabricated.
Now, let us discuss the deposition methods and processing conditions followed for each layer in detail.

### 4.2 7059 Glass Cleaning

The 7059 glass substrates were first cleaned by the following procedure before being used for processing:

- The glass substrate was first washed in De-ionized (DI) water for a few seconds and a small brush was used to remove dust particles from the surface of the glass.
- The glass was then dipped in dilute Hydrofluoric (HF) acid for a few seconds to etch off a very thin layer of glass, thus leaving behind a clean and smooth surface.
- The glass was finally rinsed in DI water and blown dry using dry nitrogen.

Glass substrates cleaned by this procedure were then ready for further processing.

### 4.3 Transparent Conducting Oxide (TCO) Deposition

#### 4.3.1 Tin Oxide (SnO\textsubscript{2}) Deposition

Tin Oxide (SnO\textsubscript{2}) was deposited by Metal Organic Chemical Vapor Deposition (MOCVD) technique in a bi-layer form. The MOCVD chamber set up is shown in figure 38. Tetramethyl Tin (TMT) was used as the source of tin. First, a doped layer of SnO\textsubscript{2}:F was deposited using a fluorocarbon 13B1 as a source of fluorine (Dopant), followed by a layer of undoped SnO\textsubscript{2}. A layer of high resistivity SnO\textsubscript{2} was then deposited because it has been shown that this layer helps in increasing the device yield and also improves the cell stability under
stress conditions[13]. The precursor TMT reacts with oxygen as shown in the equation,

$$(\text{CH}_3)_4\text{Sn}(g) + 8\text{O}_2 \rightarrow \text{SnO}_2 + 6\text{H}_2\text{O}(g) + 4\text{CO}_2$$

During one deposition process, SnO$_2$ was deposited on 4 glass substrates that were placed on a graphite susceptor as shown in figure 38. The graphite susceptor on which the glass substrates were placed was RF heated to a substrate temperature of 470°C. Ultra High Purity (UHP) Helium was used as the carrier gas during the deposition process. The graphite susceptor was usually inclined at a few degrees to avoid reactant depletion effects i.e., to avoid the reduction in thickness of SnO$_2$ with distance, along the graphite susceptor[38]. The sheet resistance, $R_s$ of the films normally ranged from 8 – 10 $\Omega/\square$. 

Figure 38 MOCVD Chamber
4.3.2 Zinc Oxide (ZnO) Deposition

Zinc Oxide (ZnO) was deposited by RF sputtering using a ZnO target. The chamber set up used in the deposition of ZnO is shown in figure 39. The samples to be deposited with ZnO were loaded on to a graphite plate which acts as the substrate holder. The chamber was then pumped down to a base pressure of $10^{-5}$ Torr and then Argon (Ar) was backfilled to the desired deposition pressure. RF power was then supplied to the target and the LC tuner was either auto tuned or manually tuned until the plasma stream hit the substrate. The substrate was rotated continuously to ensure uniform deposition of the film. The deposition conditions used are summarized using the following table.
### Table 2 Processing Conditions for ZnO Deposition

<table>
<thead>
<tr>
<th>Target</th>
<th>ZnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition Pressure</td>
<td>2 mTorr</td>
</tr>
<tr>
<td>Deposition Ambient</td>
<td>Ar</td>
</tr>
<tr>
<td>Deposition Temperature</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>Thickness</td>
<td>~3000 Å</td>
</tr>
</tbody>
</table>

### 4.3.3 Zinc Stannate (Zn₂SnO₄) Deposition

Zinc Stannate (Zn₂SnO₄) was deposited by RF co-sputtering using Zinc Oxide (ZnO) and Tin Oxide (SnO₂) targets in the same chamber that was used for the deposition of ZnO. Zn₂SnO₄ was deposited on SnO₂ to act as a high resistive buffer layer. The same deposition procedure was followed here except that two targets i.e., ZnO and SnO₂ were used for deposition of the Zn₂SnO₄ film. The deposition rates of ZnO and SnO₂ were adjusted to obtain stoichiometric Zn₂SnO₄ films. The deposition conditions used are summarized using the following table.

### Table 3 Processing Conditions for Zn₂SnO₄ Deposition

<table>
<thead>
<tr>
<th>Target 1</th>
<th>SnO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target 2</td>
<td>ZnO</td>
</tr>
<tr>
<td>Deposition Pressure</td>
<td>2 mTorr</td>
</tr>
<tr>
<td>Deposition Ambient</td>
<td>Ar</td>
</tr>
<tr>
<td>Deposition Temperature</td>
<td>Room Temperature</td>
</tr>
<tr>
<td>Thickness</td>
<td>1000 Å</td>
</tr>
</tbody>
</table>
4.4 Cadmium Zinc Telluride (Cd$_{1-x}$Zn$_x$Te or CZT) Deposition

Cadmium Zinc Telluride, which is the absorber layer, was deposited by the Close Spaced Sublimation (CSS) technique. The advantages of this method over other methods are as follows.

- Low Cost
- Simple equipment set-up
- High deposition rates
- Efficient material utilization

The experimental set-up of CSS technique is shown in figure 40. The source material used were 99.999 % pure 3 – 4 mm CdTe and ZnTe chunks placed alternatively in a graphite boat which acted as the source. The substrate was in contact with another graphite block (substrate holder) and both, the source and the substrate were separated from each other using spacers that were 5-7 mm thick. After the sample was loaded inside the chamber, ultra high purity Helium (He) was filled in and pumped out three to four times to remove any impurity gases from the chamber. Then the gas to be used as the deposition ambient was filled in and pumped out twice and was backfilled to the desired deposition pressure. Tungsten halogen lamps were used to heat the source and the substrate to the desired temperature during deposition.
The thickness of the CZT films deposited was mainly dependent on the following parameters.

- Temperature of source and substrate
- Deposition ambient
- Deposition pressure
- Time of Deposition
- Ratio of CdTe and ZnTe chunks placed in the graphite boat
- Spacing between source and substrate

The amount of CdTe and ZnTe chunks placed on the graphite boat was controlled in the ratio of 1:10 to achieve CZT films with bandgaps of ~ 1.6 – 1.7 eV. The processing conditions used in the deposition of CZT films can be summarized using the following table.
Table 4 Processing Conditions for CZT Deposition

| Temperature of Source ($T_s$) | 630 - 660°C |
| Temperature of Substrate ($T_{sub}$) | 500 - 560°C |
| Deposition Ambient | Helium (He) |
| Deposition Pressure | 1 - 5 Torr |
| Deposition Time | 5 - 10 min |
| Spacing between Source and Substrate | 5 - 7 mm |

4.5 CZT Film Annealing

Some of the as deposited CZT films were subject to annealing before applying the back contact. The annealing experiments were performed in the same CSS chamber used for CZT film deposition. The as deposited CZT film was placed on a graphite substrate holder and loaded in the chamber. The same procedure of filling in and pumping out of He followed for CZT film deposition was also followed here. The chamber was then backfilled to the required pressure with the gas to be used as the annealing ambient. The sample was then heated using the tungsten halogen lamps for the required amount of time.

4.6 Back Contact Processing

Graphite paste mixed with HgTe:Cu was used as the back contact material for the CZT solar cells. The cell areas were first defined by applying thin strips of Kapton tapes on the CZT film. The doped graphite paste was then applied on the CZT film with the
help of a brush or a spatula and the substrates were kept in a dessicator overnight. The
tapes were then removed and the CZT film around the cells was scribed off exposing the
SnO₂ surface. The cells were then annealed at 225°C in He ambient for 25min. I-V and
spectral response measurements were normally carried out after contact annealing.

4.7 CZT Solar Cell Measurements

As discussed earlier, the CZT solar cells were characterized using I-V and
Spectral Response measurements. Let us discuss in detail about these measurements in
the following sections.

4.7.1 I-V Measurements

I-V measurements were done using an AM 1.5 Solar Simulator. 300 W
photo optic lamps were used as the source of light. The intensity of the lamps
were controlled by rheostats to simulate AM 1.5 conditions. Copper probes were
used as the contact for the front and back contact (SnO₂ and Graphite) of the solar
cell. Light generated was measured by biasing each solar cell from a negative to
positive (-2 to +2 V normally) voltage after turning on the lamps. Short Circuit
Current (Iₚₑ) was calculated by dividing the current generated by the area of the
device. I-V curves were drawn by plotting the voltage against the short circuit
current.

4.7.2 Spectral Response Measurements

Spectral Response measurements were done using an Oriel
Spectrophotometer. Quantum efficiency is the measure of how efficiently a
device converts the incoming photons to charge carriers. The quantum efficiency
of each cell was measured as a function of the wavelength of the incident light.
The spectral response setup uses a 400 W tungsten halogen lamp as the light source. A monochromator with gratings and a slit was used to produce a monochromatic beam of light. A series of mirrors were used inside the monochromator to focus a small spot of light on the solar cell. Copper probes were used as contact for the solar cells to measure the generated current from the back contact. The measurements were performed with the help of a computer which uses Labview software program to control the monochromator. The procedure was run between a selected wavelength range and the quantum efficiency and current generated were calculated using a predefined spreadsheet. The spectral response was obtained by plotting the wavelength against the quantum efficiency.
CHAPTER 5

RESULTS AND DISCUSSION

The device structure of the CZT solar cell used in this research work is of superstrate configuration (figure 41) as discussed in the previous chapter. TCO was first deposited on a clean 7059 glass substrate which was then followed by CZT deposition by CSS technique.

![Figure 41 CZT Solar Cell Structure]

The different types of TCO’s used in this research work have already been discussed in the previous chapters. Following the CZT deposition, the films were annealed in different temperatures and were then contacted. I-V and Spectral Response (SR) measurements were performed on the fully fabricated devices.
5.1 Optimization of CZT Film Thickness

As discussed in chapter 4, CdTe and ZnTe chunks were used as the sources for CZT film deposition by the CSS technique. CdTe and ZnTe chunks measuring 2-3 mm were placed alternatively on the graphite boat which acted as the source. CZT was deposited on SnO₂ during the thickness optimization process. The deposition conditions used for CZT film deposition are summarized by the following table.

Table 5 CZT Deposition Conditions for Thickness Optimization

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of Source</td>
<td>660°C</td>
</tr>
<tr>
<td>(T₁,₀)</td>
<td></td>
</tr>
<tr>
<td>Temperature of Substrate</td>
<td>550°C</td>
</tr>
<tr>
<td>(T₂,₀)</td>
<td></td>
</tr>
<tr>
<td>Deposition Ambient</td>
<td>Helium (He)</td>
</tr>
<tr>
<td>Deposition Pressure</td>
<td>5 Torr</td>
</tr>
<tr>
<td>Deposition Time</td>
<td>5 min</td>
</tr>
<tr>
<td>Spacing between Source</td>
<td>7 mm</td>
</tr>
<tr>
<td>and Substrate</td>
<td></td>
</tr>
</tbody>
</table>

After CZT deposition, the film was scribed at various positions along the edges and center until the SnO₂ surface was exposed. The thickness measurements were done using a Dektak Profilometer. Figure 42 shows the approximate positions where the thickness measurements were done on the CZT film along with the thickness values in a table.
Figure 42 Thickness of CZT Film at Various Positions

As seen from the picture, the thickness of the CZT film reduced considerably along the edges. The reasons for this effect were believed to be the following.

- Lack of enough source material along the edges of the graphite susceptor.
- The sublimed material escaped form the source along the sides and got deposited along the edges of the graphite substrates due to very high spacing between the source and the substrate.

In subsequent runs, these issues were resolved by stacking more material along the edges of the graphite susceptor and by reducing the spacing from 7 mm to 4.5 mm.

5.2 SnO₂/CZT/Graphite Device Structure

Solar cells as shown in figure 41 were fabricated with SnO₂ as the TCO layer. Cadmium Zinc Telluride was deposited with a source and substrate temperature of 660°C and 550°C in 5 Torr He for 10 min. The thicknesses of the CZT films measured were in the range of 4-5.5 µm. Optical measurements were done on these films using an Oriel
Spectrophotometer to determine the transmittance and bandgap of the CZT films. The transmission response of one of the CZT films deposited on SnO$_2$ is shown in figure 43.

![Figure 43 Transmission Response of CZT on SnO$_2$](image)

We can see that the CZT film shows a sharp absorption edge at ~710-730 nm. All the CZT films deposited on SnO$_2$ had an average transmission of 55 - 60%. The optical bandgap of the films was determined by plotting the square of the absorption coefficient against the photon energy[39]. The absorption coefficient $\alpha$ was determined by using the following relation,

$$I = I_o e^{-\alpha x}$$

Where,

$I_o$ is the incident light intensity
I is the intensity of light transmitted through the film

x is the thickness of the film

A plot of $\alpha^2$ vs. photon energy used to determine the bandgap is shown in figure 44. The bandgap is found by extrapolating the curve to the x-axis.

Figure 44 Bandgap of a CZT Film on SnO$_2$ ($E_g = \sim 1.67$ eV)

The bandgap of the CZT films was always from 1.6 to 1.7 eV as that is the ideal bandgap required by the top cell absorber material in a tandem solar cell to have efficiencies of around 25%.
XRD measurements were also done on the CZT films to determine the crystalline orientation using a Philips X’Pert X-Ray Diffractor. Figure 45 shows the XRD pattern of a CZT film on SnO$_2$.

![XRD Pattern of CZT on SnO$_2$](image)

Figure 45 XRD Pattern of CZT on SnO$_2$

We can see that the CZT film shows preferred (111) orientation. The absence of CdTe and ZnTe peaks indicate that the CZT films obtained were of single phase. This preferential orientation was observed for all CZT films deposited at the substrate temperature of 540°C or above.

SEM measurements were done on the films to determine the surface morphology by using a Hitachi S-800 Secondary Electron Microscope.
Figure 46 shows the SEM image of a CZT film deposited on SnO₂. We can see that the grains are relatively densely packed.

The SnO₂/CZT devices discussed in this section and section 5.3 have been grouped into three types based on the CZT film annealing as follows.

Type A - As-deposited CZT film.

Type B - CZT film annealed in Hydrogen (H₂) ambient at 400°C for 15 min.

Type C - CZT film annealed in Helium and Oxygen (He + O₂) ambient at 400°C for 15 min.

Type A devices had $V_{oc}$’s in the range of 180 – 240 mV and $J_{sc}$’s in the range of 8 – 10 mA/cm². Type B devices had $V_{oc}$’s in the range of 170 – 210 mV and $J_{sc}$’s in the range of 8 – 9 mA/cm² while Type C devices had $V_{oc}$’s in the range of 20 – 50 mV and almost negligible $J_{sc}$’s. The poor performance of the Type C devices was due to the oxidation of
the CZT film during annealing (annealed in He+O₂) which resulted in poor ohmic contact with the back contact material. One of the reasons for poor $V_{oc}$’s and $J_{sc}$’s could also be due to the CZT film being resistive. The Fill Factor (FF) for all the three types of devices was from 25 to 40 %. The reduction in FF was mainly due to the high series resistance and shunting issues present in the device. The series and shunt resistances of these devices were in the range of 20 – 30 $\Omega$ and 300 – 500 $\Omega$. Table 6 shows the best cell in all the three types of devices.

Table 6 Best Device for SnO₂/CZT/Graphite Device Structure

<table>
<thead>
<tr>
<th>Type</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A</td>
<td>240</td>
<td>10.04</td>
</tr>
<tr>
<td>Type B</td>
<td>210</td>
<td>9.53</td>
</tr>
<tr>
<td>Type C</td>
<td>50</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Of all the device types, Type A devices performed well with the highest current of 10.04 mA/cm² as shown in table 6. The dark and light I-V curve of these devices is shown in figure 47. All the device structures seemed to have very high series resistance. Figure 48 shows the spectral response of the three types of devices. We can see that Type C device has a very low response as compared to the other two types. Type A and B devices have good collection at the shorter wavelengths, but the collection in the CZT bulk decreases at longer wavelengths.
Figure 47 Dark and Light I-V Curves for SnO$_2$/CZT/Graphite Device Structure

Figure 48 Spectral Response for SnO$_2$/CZT/Graphite Device Structure ($E_g = 1.62 \text{ eV}$)
5.3 SnO$_2$/CZT (Br/CH$_3$OH etched)/Graphite Device Structure

In this type of structure, the CZT films were Br/CH$_3$OH etched before contacting similar to the procedure followed in CdS/CdTe solar cells, to make the film more Te rich. Table 7 shows results from the best cell in all the three types of devices.

Table 7 Best Device for SnO$_2$/CZT (Br/CH$_3$OH etched)/Graphite Device Structure

<table>
<thead>
<tr>
<th>Type</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A</td>
<td>80</td>
<td>3.27</td>
</tr>
<tr>
<td>Type B</td>
<td>100</td>
<td>3.98</td>
</tr>
<tr>
<td>Type C</td>
<td>30</td>
<td>2.66</td>
</tr>
</tbody>
</table>

Figure 49 Dark and Light I-V Curves for SnO$_2$/CZT (Br/CH$_3$OH etched)/Graphite Device Structure

Figure 49 and 50 show the dark and light I-V and the spectral response of these devices. We can see that Br/CH$_3$OH etch doesn’t improve the device performance in the case of
CZT films. As discussed earlier, Br/CH₃OH etch makes the CdTe film surface more Te rich. In the case of CZT, we don’t see this effect may be due to poor transport properties in the CZT bulk after performing the etch.

![Graph](image)

Figure 50 Spectral Response for SnO₂/CZT (Br/CH₃OH etched)/Graphite Device Structure

### 5.4 SnO₂/CZT/Cu Device Structure

Device structures with Cu as the back contact were also fabricated to see the effect of back contact on CZT solar cells. Cu was deposited by RF sputtering to a thickness of about 60 Å. For this type of structure, light was shone from both sides i.e., from the glass side (superstrate structure) and from the Cu side (substrate structure) to see the device performance. The best $V_{oc}$ and $J_{sc}$ obtained for this structure were 340 mV and 0.97 mA/cm² respectively when light was shone from the glass side. The increase in $V_{oc}$
in this device structure could be due to the Cu diffusing into the CZT material and making it more p-type. This in turn would shift the Fermi level closer to the valence band which would result in better band bending thus increasing the $V_{oc}$. Figure 51 shows the spectral response for this structure.

![Figure 51 Spectral Response for SnO$_2$/CZT/Cu Device Structure](image)

From the figure, we can see that collection is poor for all wavelengths. The reason for this could be due to the copper back contact which apart from doping the CZT p-type could also diffuse all the way into the junction, hence affecting the junction properties or even shorting some of the devices.

### 5.5 SnO$_2$/Zn$_2$SnO$_4$(ZTO)/CZT/Graphite Device Structure

In this type of structure, ZTO was used as a buffer layer between the SnO$_2$ and the CZT layer. The same deposition conditions for CZT used in section 5.2 were used here.
The device structure for this type of device is as shown in figure 52. In conventional CdS/CdTe devices, a high resistive ZTO layer causes an increase in quantum efficiency in the short wavelength regions by interdiffusing with the CdS layer and increasing its bandgap due to the incorporation of zinc[40]. As results from He + O₂ annealed samples from all the device structures discussed in the previous sections did not lead to improved performance, only Type A (As Deposited CZT) and Type B (H₂ annealed) devices were fabricated on ZTO. ZTO was deposited by RF sputtering followed by annealing at 600°C for 15 minutes in He Ambient. This annealing of the ZTO film was done to make the film polycrystalline.

![Device Structure Diagram](image)

**Figure 52 SnO₂/Zn₂SnO₄(ZTO)/CZT/Graphite Device Structure**

Figure 53 shows the transmission response of a CZT film on SnO₂/ZTO. It can be seen that the addition of a ZTO buffer layer has not reduced the transmission.
The transmission response of the CZT films deposited on SnO$_2$/CZT showed an average transmission of 55 – 60 %. Figure 54 shows the dark and light I-V curve of a Type A and Type B devices. The performance of both devices types was essentially identical except
that Type B devices showed more shunting. This may be due to creation of interface defects in the CZT during H₂ annealing. The average $V_{oc}$’s and $J_{sc}$’s of Type A and Type B devices were almost the same in the range of 170 – 190 mV and 6 – 7.2 mA/cm². The graph showing the spectral response measurements of these devices is shown in figure 55. Type A devices had better collection than Type B devices at longer wavelengths as seen from figure 55. The absorption in the Type B devices dies down gradually instead of getting absorbed in the CZT bulk. This could be due to the collection losses in the CZT bulk. Table 8 shows the results of the best cell in both the type of devices.

![Figure 55 Spectral Response for SnO₂/ZTO/CZT/Graphite Device Structure](image)
Table 8 Best Device for SnO$_2$/ZTO/CZT/Graphite Device Structure

<table>
<thead>
<tr>
<th>Type</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A</td>
<td>190</td>
<td>7.24</td>
</tr>
<tr>
<td>Type B</td>
<td>190</td>
<td>7.05</td>
</tr>
</tbody>
</table>

5.6 ZnO/CZT/Graphite Device Structure

In this type of device structure, ZnO was used as the TCO instead of SnO$_2$. ZnO was chosen because of its good optical properties and large bandgap. The same deposition conditions for CZT used in section 5.2 were used here. Figure 56 shows the transmission response of CZT film on ZnO. We can see that the CZT has an average transmission of 60% with a sharp absorption edge at 710 – 730 nm. This absorption edge approximately corresponds to a bandgap of 1.65 – 1.7 eV.
The ZnO/CZT devices discussed in this section have been grouped into three types based on the CZT film processing before applying back contact.

Type A - As-deposited CZT film.

Type B - Br/CH₃ etched and contacted without undergoing any annealing step.

Type C - Deposited in Oxygen (O₂) ambient at 1 Torr for 5 minutes and contacted as-deposited without undergoing any annealing step.

The dark and light I-V curves for these types of devices are shown in figure 57. We can see that all the device types have high series resistance which could be due to the contact resistance between the back contact and the CZT layer. Another reason for the poor performance of these devices could be because of the CZT film being resistive which could lead to low Vₜₜ’s and low Jₜₜ’s. These devices also showed high shunting which
could be due to interface defects present in the CZT material. Figure 58 shows the spectral response for the three types of devices. All the three device types had collection losses in the longer wavelength region. The shift in the bandgap for all the three device types was due to the variation in the film properties from one end to another i.e., the cadmium content in the CZT film depletes along the edges of the sample after the source has been used for four to five times. Table 9 shows the performance of the best cell in all the three types of devices.

Figure 57 Dark and Light I-V Curves for ZnO/CZT/Graphite Device Structure
Figure 58 Spectral Response for ZnO/CZT/Graphite Device Structure

Table 9 Best Device for ZnO/CZT/Graphite Device Structure

<table>
<thead>
<tr>
<th>Type</th>
<th>$V_{oc}$ (mV)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type A</td>
<td>130</td>
<td>6.98</td>
</tr>
<tr>
<td>Type B</td>
<td>80</td>
<td>5.09</td>
</tr>
<tr>
<td>Type C</td>
<td>80</td>
<td>3.96</td>
</tr>
</tbody>
</table>
CHAPTER 6

CONCLUSIONS

Cadmium Zinc Telluride, Cd$_{1-x}$Zn$_x$Te (CZT) was successfully deposited by the CSS technique on various transparent conducting oxides like SnO$_2$, ZnO and ZTO. The CZT films were annealed at different temperatures to study the effect of annealing. I-V and spectral response measurements were done to study the performance of CZT solar cells. CZT films deposited by the CSS technique had an average transmission of 55 – 60 % and a bandgap of 1.6 – 1.7 eV. The films were 4.5 -5 µm thick.

SnO$_2$/CZT/Graphite device structures had the best overall performance in terms of J$_{sc}$’s. The fill factors for all the device structures averaged from 30 – 50 %. The Type A (As Deposited) devices performed better than the Type B (H$_2$ Annealed) or Type C (He + O$_2$ annealed) devices. These devices had J$_{sc}$’s from 8 – 9 mA/cm$^2$ with the best device having a J$_{sc}$ of 10.04 mA/cm$^2$ (Type A). The V$_{oc}$’s were however low with the best device having a V$_{oc}$ of 240 mV (Type A).

SnO$_2$/CZT(Br/CH$_3$OH etched)/Graphite device structures had J$_{sc}$’s in the range of 2 – 3.5 mA/cm$^2$ and V$_{oc}$’s from 30 – 100 mV. All three types of devices (Type A, Type B and Type C) had poor V$_{oc}$’s and J$_{sc}$’s. Type B (H$_2$ Annealed) devices had the best performance in this device structure with a J$_{sc}$ of 3.98 mA/cm$^2$. 

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SnO\textsubscript{2}/CZT/Cu device structures had $V_{oc}$’s in the range of 250 – 340 mV, but the $J_{sc}$’s were low in the range of 0.5 - 1 mA/cm\textsuperscript{2}. The best device had a $V_{oc}$ of 340 mV and $J_{sc}$ of 0.9 mA/cm\textsuperscript{2}.

SnO\textsubscript{2}/ZTO/CZT/Graphite device structure had $J_{sc}$’s from 5 – 7 mA/cm\textsuperscript{2} with the best device having a current of 7.24 mA/cm\textsuperscript{2}. The $V_{oc}$’s were low in the range of 170 – 190 mV. The Type A (As Deposited) devices performed better when compared to the Type B (H\textsubscript{2} Annealed) devices.

ZnO/CZT/Graphite device structures also had good $J_{sc}$’s with the best device having a current of 6.98 mA/cm\textsuperscript{2}. Cells made from CZT films deposited in O\textsubscript{2} ambient (Type C) had very poor performance. Type A (As Deposited) devices performed better than the Type B (As Deposited [Br/CH\textsubscript{3}OH Etched]) devices.
REFERENCES


