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Indium Oxide as a High Resistivity Buffer Layer for CdTe/CdS Thin Film Solar Cells

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Indium Oxide as a High Resistivity Buffer Layer for CdTe/CdS Thin Film Solar Cells

by

Umamaheswari Balasubramanian

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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March 24, 2004

Keywords: TCOs, front contact, optical properties.

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DEDICATION

This Thesis is dedicated to my family and my loving husband Rajender, without whose help and support, I would not have been able to complete my thesis.
ACKNOWLEDGEMENTS

I am indebted to my major professor Dr. Chris Ferekides, who gave me this wonderful opportunity to do my masters under his meticulous guidance. I am very grateful to Dr. Robert Mamazza, Jr., for always being there for me, right from getting me started in research and helping me through out the course of this program. I also like to thank my other committee members Dr. Don Morel and Dr. Andrew Hoff for their valuable time and consideration.

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INDIUM OXIDE AS A HIGH RESISTIVITY BUFFER LAYER IN CDTE/CDS
THIN FILM
SOLAR CELLS
Umamaheswari Balasubramanian

ABSTRACT

Transparent conductive oxides are an essential part of technologies that require both large-area electrical contact and optical access in the visible portion of the light spectrum.

SnO₂ doped with Fluorine (SnO₂: F) and In₂O₃ doped with tin (ITO) are the most popular choices of front contacts for CdTe solar cells. In this thesis, CdS/CdTe devices were fabricated with SnO₂: F (MOCVD) and ITO (sputtering) as front contacts without a high resistivity (resistivity relatively greater than front contact) buffer layer. The device characteristics of these devices were low but improved considerably after the inclusion of an intrinsic SnO₂ (SnO₂-i) deposited by MOCVD as buffer. Thus having emphasized and demonstrated the benefits of a buffer layer in these devices, the use of reactively sputtered SnO₂ (intrinsic), SnO₂ doped with Zinc (5% and 10% Zinc) and In₂O₃(intrinsic) as buffer layers in SnO₂:F/buffer/CdS/CdTe devices were explored.

Experiments were also carried out on the photovoltaic active layers of SnO₂:F/SnO₂-i/CdS/CdTe Solar cells. Namely, the effect of window layer thickness was studied by making a series of devices in which the CdS thickness was progressively reduced and the effect of substrate temperature (T_sub) during the deposition of the absorber layer was also studied by increasing T_sub > 600°C during CdTe CSS.

In order to determine the effectiveness of In₂O₃ as a buffer layer, a series of ITO/In₂O₃/CdS/CdTe cells were fabricated with varying thickness of In₂O₃ (250 to 2000 Å) and also the CdS thickness was reduced in steps (~800 Å to~500 Å) in these devices.
ITO/In$_2$O$_3$ device with efficiency greater than 14% (Voc: 820 mV, FF: 72% and $J_{sc}$: 24 mA/cm$^2$) was fabricated for an In$_2$O$_3$ thickness of 250 Å and CdS thickness of ~600 Å. However the best efficiency of 14.7% (Voc: 830 mV, FF: 77%, $J_{sc}$: 23 mA/cm$^2$) was achieved for SnO$_2$:F/SnO$_2$-i/CdS/CdTe device.

ITO films with resistivity as low as $1.9 \times 10^{-4}$ Ω-cm, mobility 32 cm$^2$V$^{-1}$s$^{-1}$ and average transmission ~90% in the visible region were obtained for carrier concentration in the order of $1.1 \times 10^{21}$ cm$^{-3}$. 
CHAPTER 1
INTRODUCTION

Most of the energy that we use in the day to day life comes from fossil fuel and nuclear power stations. In energy terms, oil makes the single largest contribution to world energy supply, at forty percent, followed by coal at twenty six percent and natural gas at about twenty four percent. When these fossil fuels are being burnt, harmful emissions are being released into the environment. These include carbon and sulphurdioxides which contribute to climate change and acid rain. Some of the effects due to the pollution caused by combustion of these fossil fuels are the green house effect and the depletion of the atmospheric ozone layer. Non-renewable, fossil fuels take millions of years to form, so they are finite and, ultimately, exhaustible energy resources.

Figure 1. Solar Power [2].

On the other hand, there are serious doubts surrounding the safety of nuclear technology and how to dispose of the radioactive waste products. Therefore, we must develop and use alternative energy resources.
Over the last twenty years there have been major steps in the development of renewable energy technology for both industry and domestic use. As the amount of sunshine energy that reaches the surface of the Earth every minute is greater than the total amount of energy that the world's human population consumes in a year, the sun is our only long-term natural resource. The earth’s atmosphere and clouds absorb, reflect and scatter some of the radiation from the sun nonetheless enormous amounts of direct and diffused sunlight energy reaches the earth which can be converted to electricity. Photovoltaic devices that directly convert the sunlight into electricity are called solar cells. Solar cells are considered a major candidate in providing nearly permanent power at low operating cost. The major drawback of solar cells at present is the high manufacturing cost involved. So research has to be done to improve device structure and reduce the manufacturing costs. Solar cells at present furnish the most important long-duration power supply for satellites and space vehicles. Solar cells have also been successfully employed in small to medium scale terrestrial applications.

1.1 Photovoltaic Effect and Origin of Solar Cells

The photovoltaic effect is the phenomenon by which solar cells convert sunlight into electricity. Sunlight comprises packets of energy called photons. In 1839, a nineteen year old Henry Becquerel discovered that electric current could be produced by shining light onto certain chemical solutions. In 1877, this effect was observed in a solid material, Selenium for the first time. Practical solar cells have been made only since the mid 1950s after Einstein in 1905 and Schottky in 1930 provided a deeper insight into the understanding of the scientific principles involved in solid state physics.

A silicon solar cell which converted 6% of sunlight incident upon it into electricity was developed by Chapin, Pearson and Fuller in 1954 and cells of this kind were used in space applications in 1958. Now solar cells with more than 30% of efficiency are being produced [2, 3].

1.2 Principle of Operation of Solar Cells

Solar cells, in the simplest form are p-n junction devices which use sunlight to create electrical energy.
The Fermi Level is a theoretical level derived from the Fermi-Dirac electron distribution in a solid that defines an electron’s probability of occupying a specific energy level or state. The Fermi level also defines the magnitude of energy required to remove an electron from a semiconductor into free space (or the vacuum level in a band diagram), which is the work function of the material. In intrinsic materials, the Fermi level is approximately centered between the conduction band and the valence band. For n-type materials, it is shifted up towards the conduction band; for p-type materials, it is shifted downwards towards the valence band.

![Diagram of Fermi Level Positions of P-type and N-type Semiconductors](image1.png)

**Figure 2. The Fermi Level Positions of P-type and N-type Semiconductors.**

When a p-type semiconductor and n-type semiconductor are brought together, the Fermi levels get lined up, causing band bending in valence and conduction band. Electrons from the n-side combine with the holes on the p-side resulting in a positive charge on the n-side of the junction and a negative charge accumulation on the p-side. This separation of charge creates a junction potential or built-in potential, and is denoted $V_{bi}$ [1].

![Diagram of Bending of Valence and Conduction Band due to Fermi Level Lining Up](image2.png)

**Figure 3. Bending of Valence and Conduction Band due to Fermi Level Lining Up.**
In Figure 3, the built-in potential \( qV_{bi} \) is defined as the difference in the relative energies of the conduction bands between the p-type and the n-type materials on either side of the junction. When a photon, with energy greater than the band gap of the semiconductor, passes through the solar cell, it may be absorbed by the material. This absorption takes the form of a band-to-band electronic transition, so an electron/hole pair is produced. If these carriers can diffuse to the depletion region before they recombine, then they are separated by the electric field, causing one quantum of charge to flow through an external load. This is termed as photovoltaic effect. The current thus produced is termed as photocurrent (see figure 4).

**Figure 4. Origin of Photocurrent.**

1.3 Basic Solar Cell Device Structure

As described in the previous section, a solar cell consists of a p-n junction. This junction could be made of p-type and n-type semiconductor either of the same material (homojunction) or different materials (heterojunction). A typical heterojunction is made between a wide band gap material and a narrow band gap material. There are inherent advantages and disadvantages in each of these types.
The obvious advantage of a homojunction is the perfect band alignment. Band alignments are illustrated in figure 5, which shows both a homojunction (top) and a heterojunction (bottom) at equilibrium. Also, having the same material will also result in perfect lattice match at the junction, which leads to significantly fewer interfacial traps than that in a heterojunction.

The existence of traps near the junction can reduce carrier life times. Mostly for heterojunctions, careful material selection (and or manipulation) can approximate many of the advantages of the homojunction, with some focus on reduction of lattice mismatch effects and reduce the formation of interfacial defects and knowledge of work functions and electron affinities to reduce band related effects. It should also be noted that lattice match (or mismatch) and band related issues are not solely responsible for solar cell performance, the band gap and the absorption coefficient of the absorber, among other things, are also very important. In figure 5, the heterojunction shows a band alignment discontinuity that is prominent in the conduction band minimum ($\Delta E_c$), provided this value is relatively small, the obstruction to the flow of minority carriers across the junction will be almost negligible. An important advantage a heterojunction has over its counterpart is that the window layer may have a wider band gap than the absorber.
This wider band gap will allow greater current generation from high energy photons. Further series resistance can also be lower for a heterojunction if the window layer is able to be heavily doped. These various considerations are device structure specific, and are not intended to cover all scenarios. The only modification to the p-n junction to turn it into a solar cell is the addition of appropriate contacts. One of the contacts would have to be semi-transparent to permit the light; or alternatively, it could also be a metal grid that only covered a small portion of the device. When the front contact used is a semitransparent oxide, the material used is classified as transparent conducting oxide (TCO) (as shall be discussed further in the subsequent chapters). The back contact need only be chemically and physically compatible with the adjacent material. With respect to figure 6, it can be seen that the n-type material is facing the light. So light passes through the n-type material and reaches the p-type material.

**Figure 6. Basic Structure of a Solar Cell.**

So the p-type material is referred to as absorber and it should be capable of absorbing the photons of energy equal to or greater than it’s band gap. So in this arrangement, ideally speaking both the front contact and n-type material should be large band gap devices, to prevent optical losses, which could have otherwise been converted to electricity. And the n-type material should be as thin as possible to permit most of the light to enter the p-type material. Solar cells can be manufactured in a variety of ways and with a variety of materials. They can be categorized into three main types (as shown in Table 1).
Table 1. The Summary of Different Types of Materials Used to Make Solar Cells.

<table>
<thead>
<tr>
<th>Crystalline</th>
<th>Thin Film</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline Silicon (c-Si)</td>
<td>Amorphous Silicon (a-Si)</td>
<td>Quantum dot solar cells</td>
</tr>
<tr>
<td>Gallium Arsenide (GaAs) and Alloys</td>
<td>Thin film Silicon</td>
<td>Dye sensitized photochemical cells</td>
</tr>
<tr>
<td></td>
<td>Copper Indium Diselenide (CIS)</td>
<td>Polymer cells</td>
</tr>
<tr>
<td></td>
<td>Cadmium Telluride (CdTe)</td>
<td>Photoelectrochemical Cells</td>
</tr>
</tbody>
</table>

Crystalline silicon currently makes up over 86% of the photovoltaic market. The reason for this dominance is that the material, technology, and equipment come right out of the solid state integrated circuit industry. The development of c-Si cells is very energy intensive. It is therefore very expensive to process these cells and the technology is leaning toward the production of polycrystalline Si cells and other thin film based technologies.

Gallium arsenide can be alloyed with indium (In), phosphorous (P), and aluminum (Al) to produce multijunction cells with very high efficiencies. Amorphous silicon makes up most of the remaining 14% of the PV market. Cadmium telluride is a promising thin film technology. CdTe has a band gap of 1.45 eV and is therefore best suited for the solar spectrum and the material has a very high absorption coefficient, so only a micro meter of the material is enough to absorb 90% of the incident radiation. With time it is thought to be the most promising thin film to meet the cost goals needed for PV. The highest efficiency reported for CdTe solar cell is 16.4% by NREL [15] and the University of S.Florida is holding the second place with an efficiency of 15.8% [31].
CIS and its alloys is also a promising thin film material with laboratory efficiencies of 18% and module efficiencies greater than 11%. This product is currently on the market and boasts 20+ years of research and development. Another type of thin film is thin film polycrystalline silicon. This is a new technology that is in the experimental stages.

Among the “other” category include quantum dot solar cells in which a nanocrystalline CdSe semiconductor is embedded in the conductive polymer/C60 composite. This has the potential for low-cost, large-area production. Dye-sensitized photochemical cells have a dye sensitizer that absorbs light and generates electron hole pairs in a nanocrystalline titanium dioxide semiconductor layer. Only certain wavelengths can be absorbed but because the device is clear, research is being conducted to create a clear window that will absorb and convert UV light into energy [4].

1.4 Basic Solar Cell Physics

![Figure 7. The Current –Voltage (I-V) Characteristics of a P-N Junction Diode.](image)

The Current –Voltage (I-V) characteristics of a p-n junction diode for different optical stimuli are shown in the figure above.

If the p-n junction is operated in the fourth quadrant, the product of a negative current and a positive voltage will yield a negative power. Physically, this corresponds to a source of power. Consequently, a p-n junction operated in the fourth quadrant can be used as a source of power; this is the principle behind the solar cell [5].
The current and voltage relationship in a p-n junction diode can be written as

\[ I = I_o \left( \exp \frac{qV}{AKT} \right) - 1 \tag{1} \]

Where \( I_o \) is the reverse saturation current and \( A \) is an ideality factor that is introduced to modify the theoretical expression for use with "Ideal" diodes.

Under the presence of an optical stimulus, photons are absorbed to create electron hole pairs. Pairs that are generated within a diffusion length of the depletion region will be swept by the built in potential across the depletion region. Consequently, when being excited by light, a current is produced due to the optical generation of carriers. Including this generation current \( (I_L) \) in equation (1):

\[ I = I_o \left( \exp \frac{qV}{AKT} \right) - 1 \right) - I_L \tag{2} \]

Figure 7 demonstrates how optical excitation affects the I-V characteristic of the solar cell. It should be noted that a larger generation rate corresponds to a larger generation current, corresponding to a larger downward shift in the I-V. Figure 8 shows an equivalent circuit that may be used to model the behavior of a solar cell. The current generated by the photons is represented by an independent source. The two resistors shown in Figure 8 model two types of the losses in a solar cell. \( R_{\text{series}} \) is a series loss primarily due to resistive losses (contact resistance and bulk resistance).

![Figure 8. Equivalent Circuit of a "Real" Solar Cell Showing Both Shunt and Series Resistive Loss [5].](image)

The shunt resistance, \( R_{\text{shunt}} \), is used to model leakage currents. Including the effects of series resistance \( R_{\text{series}} \) and shunt resistance \( R_{\text{shunt}} \) in the current equation, the equation transforms as shown in equation 3.
Two quantities of interest for solar cells are the following: short circuit current ($I_{sc}$) and open circuit voltage ($V_{oc}$). Expressions for both $I_{sc}$ and $V_{oc}$ can be found from equation (2). The short circuit current is found by setting $V = 0$ in equation (2). This results in the following expression for $I_{sc}$:

$$I_{sc} = I_L$$

(4)

Similarly the open circuit voltage can be found by letting $I = 0$ in equation (2) and solve for $V$:

$$V_{oc} = \frac{AKT}{q} \ln\left[\frac{I_L}{I_o} + 1\right]$$

(5)

Under short circuit conditions, the photo generated charges flow through the external circuit and no charge build up is produced, hence no voltage is developed. The photo generation current is directly proportional to the intensity of the sunlight. Under direct sun conditions, the $I_{sc}$ is at its maximum.

Under open circuit conditions there is a charge buildup on each side creating a diode current. The device reaches equilibrium when the diode current is equal and opposite to the photo generation current. In order for the diode current, otherwise referred to as the internal or injection current, the internal potential barrier (voltage) is lowered. This further demonstrates the forward bias characteristics. Figure 9 below demonstrates the short circuit condition and Figure 10 open circuit condition [4].

$$I = I_o \left[ \exp\left(\frac{q(V - IR_{series})}{AKT}\right) - 1 \right] + \left[\frac{V - IR_{series}}{R_{shunt}}\right] - I_L$$

(3)
Figure 9. Solar Cell Under Short Circuit Condition.

Ideally the $R_{\text{shunt}}$ of a solar cell needs to be infinite and the $R_{\text{series}}$ be zero but real devices have $R_{\text{shunt}}$ in the order of several thousand ohms and $R_{\text{series}}$ in the order of 1-2 $\Omega$.

Figure 10. Solar Cell Under Open Circuit Condition.
A method to find the series resistance used by B.E.McCandless, et al., when $R_{shunt}$ can be neglected, is as follows and is derived from plotting $dV/dJ$ against $1/J$, where the intercept through the y-axis yields the series resistance and the slope provides the diode factor. Here $J$ is the current density (Amperes/cm$^2$), which can be substituted for $I$ in the above equations when the area of the device is taken into account. Substituting $J$ for all $I$ in equation (3) and treating $R_{shunt}$ (shunt resistance of the device) as negligible, we get

$$\frac{J + J_L}{J_o} + 1 = \exp \left( \frac{q(V - JR_{series})}{AkT} \right)$$

(7)

Taking the natural log on both sides

$$\ln \left( \frac{J + J_L}{J_o} + 1 \right) = \frac{q(V - JR_{series})}{AkT}$$

(8)

Solving for $V$ in the above equation,

$$V = IR_{series} + \frac{AkT}{q} \ln \left( \frac{J + J_L}{J_o} + 1 \right)$$

(9)

Differentiating $V$ with respect to $J$ we get

$$\frac{dV}{dJ} = R_{series} + \frac{AkT}{q} \left( \frac{1}{J + J_L} \right)$$

(10)

For a solar cell which is not under illumination (or in the dark) in the above equation, we could simply remove $J_L$(light generated current).

$$\frac{dV}{dJ} = R_{series} + \frac{AkT}{q} \left( \frac{1}{J} \right)$$

(11)

The above equation is in the slope intercept form: $y=b+mx$. So, from a plot of $dV/dJ$ Vs $1/J$, the y-intercept provides $R_{series}$ and from the slope the diode factor can be obtained.

However, an approximation of series resistance can be obtained from the slope of a J-V curve at high current values in the first quadrant; $dV/dJ$ when $J \to \infty$ and similarly, the $R_{shunt}$ can also be obtained from the third quadrant, $dV/dJ$ at large reverse bias. If the forward J-V characteristics of a device are influenced by barriers, then $R_{series}$ cannot be calculated reliably by this method and if the reverse bias is affected by collection, then $R_{shunt}$ cannot be found out reliably.
Another characteristic property of solar cells of interest is the fill factor, FF, which is defined as:

\[
FF = \frac{I_m V_m}{I_{sc} V_{oc}} = \frac{P_{\text{max}}}{I_{sc} V_{oc}}
\]

where \(I_m, V_m\) are the current and Voltage associated with maximum power generation. It is a measure of quality of the cell.

The efficiency is a measure of the maximum power over the input power.

\[
\epsilon = \left( \frac{P_{\text{max}}}{P_{\text{in}}} \right) 100\%, \text{ where}
\]

\(P_{\text{in}}\) is the power due to the photons incident on the cell, given by:

\[
E = \int N_{\text{photons}} h \left( \frac{c}{\lambda} \right) d\lambda
\]

where \(N_{\text{photons}}\) is the number of photons incident on the surface of the solar cell, \(h\) is Planck’s constant, \(c\) is the velocity of light and \(\lambda\) is the wavelength associated with the photons.

The energy of the sun is created by nuclear fusion reaction of hydrogen to helium. The gaseous surface of the sun radiates like a black body at 5900K. The radiation power density outside the atmosphere is known as the solar constant and it has a value of 1.353 kW/m². This radiation density at sea level is weakened by absorption and scattering in the atmosphere. In the infrared region there is absorption due to water and carbon dioxide in the air, in the visible region absorption is caused mainly by oxygen, in the ultraviolet spectral range there is interaction with the ozone in the air. AM 0 or AM 1.5 defined in the figure 11 are standards defining specific solar radiation conditions. AM (air mass) indicates the amount of air, the radiation passes through the atmosphere. AM 0 defines the intensity of extraterrestrial solar radiation (in the space), AM 1 defines the intensity of radiation incident vertically at equator and AM 1.5 defines the intensity of sunlight with the sun is positioned at an angle of 41.8° above the horizon. For terrestrial photovoltaics the standard to determine the efficiency of solar cells is AM1.5 global.
The fill factor can then be rewritten as: \( \frac{V_{oc} FFI_{sc}}{EA} \) or simply \( V_{oc} FFJ_{sc} \) (15)

In figure 12, fourth quadrant of the IV-characteristics of a solar cell under illumination is depicted with the points where Voltage and Current are maximum \( V_m, I_m \) respectively [4]. The fill factor is the ratio of the area of maximum power rectangle to the area covered by \( V_{oc} I_{sc} \).
CHAPTER 2
TRANSPARENT CONDUCTIVE OXIDES

In this chapter the properties of transparent conductive oxides (TCO) and a brief discussion of research on TCOs is reviewed.

2.1 Transparent Conductive Oxides

A TCO is a wide band gap semiconductor, and as the name implies has an inherent relative transparency in the visible region and it is highly conductive due to the presence of relatively higher concentration of free electrons in its conduction band. These arise either from defects in the material or from extrinsic dopants, the impurity levels of which lie near the conduction band edge. The high electron carrier concentration can cause absorption of radiation in both the visible and infra-red portions of the spectrum. A TCO is a compromise between electrical conductivity and optical transmittance, a careful balance between the properties is required.

2.1.1 Optical Properties

Photons incident on TCOs are absorbed, transmitted or reflected. A TCO absorbs some portion of the light incident upon it, corresponding to its band gap. TCOs with band gap less than 3.0eV tend to appear yellow-green, which corresponds to a wavelength of about 400nm. Such coloration is a function of an electron transition from the valence band to conduction band that is the band gap. These absorptions are a function of both the band gap and the thickness of the material. The relation can be described in terms of the absorption coefficient $\alpha$, which is defined as

$$\alpha(h\nu) = C(h\nu - E_g^d)^{1/2}$$  \hspace{0.5cm} (16)

where $h\nu$ corresponds to the energy of the photon, $E_g^d$ is the direct band gap of the material and $C$ is essentially a constant. A plot of $\alpha^2$ as a function of $h\nu$ yields a straight line for a direct absorption, with an intercept on the photon energy axis equal to the direct band gap of the material [32].
\( \alpha \) at a particular wavelength can also be expressed in terms of thickness of the material \( t \) and absorption \( A \) at that particular wavelength as follows.

\[
\alpha(\lambda) = \left( \frac{1}{t} \right) \ln\left( \frac{1}{1 - A(\lambda)} \right) \tag{17}
\]

For a TCO to be suitable for applications in solar cells, it is desirable that it has large band gap, greater than 3.0 eV.

**Figure 13. Possible Photon Interactions with a TCO.**

The total transmission in a TCO is given as

\[
\%T_{\text{Diffuse}} + \%T_{\text{Specular}} = \%T_{\text{Total}} \tag{18}
\]

where specular and diffuse transmission are defined in figure 13.

Absorption is associated with the band gap. Since TCOs are wide band gap semiconductors, the energy corresponding to this absorption is large; typically in the ultraviolet region, or in the near UV region. Generally transmission, both specular and diffuse, occurs in the visible region. Below the band gap of the TCO, the radiation is typically transmitted with the only “losses” being primarily due to reflection from the surface of the TCO.

The portion of the solar spectrum of wavelengths from 300 to 1000nm is most crucial to the characterization of TCOs and also critical to the photovoltaic device performance.
Figure 14. Photon-TCO Interaction Types by Characteristic Wavelength Region.

Reflection of a photon, in a TCO can take place in two ways. One is that the photon can be reflected from the surface of the material; the second is that the photon can be reflected from the bulk of the material. The greatest level of reflection occurs in the near infra red region. This reflection is dominated by bulk reflection that occurs as result of photon-electron interactions, which induce scattering. The electrons and photons react due to the electro-magnetic nature of the photon. The point at which this takes place is termed as the plasma frequency. The word plasma is used because the electrons behave as a gas in highly doped TCOs (as they do in metals). The reflection in the infra red is highly dependent on carrier concentration. Heavily doped materials have increased amount of reflection in this region.

2.1.2 Electrical Properties

Most of the semiconductor oxide films have n-type conductivity. The high conductivity of these films mainly results from stoichiometric deviations. The TCOs are also heavily doped to make them more conductive [6]. A TCO must necessarily represent a compromise between electrical conductivity and optical transmittance, a careful balance between the properties is required. Since conductivity is given as $\sigma = \mu e N$, where $\mu$ is the mobility of the carriers in a TCO, $e$ is electronic charge and $N$ is the carrier concentration. This gives one two ways to increase the conductivity of a material: 1. by increasing carrier concentration ($N$) and 2. by increasing the mobility ($\mu$). Increasing the
former also leads to an increase in free carrier absorption. Increasing the mobility does not however have any delirious effects and is therefore the focus of most research.

Having emphasized the importance of the electrical properties of a TCO in the preceding paragraph, methods to find the resistivity, carrier concentration and mobility of TCOs are discussed below.

Electric current in a conductor is defined as how much charge passes through an arbitrary cross section of a conductor in a specific amount of time. This can be represented mathematically as

\[ I = \frac{dq}{dt} \]  

(19)

Where \( I \) is the current in amperes, \( q \) is the charge in coulombs and \( t \) is time in seconds.

The current density, \( J \) can be expressed as the ratio of current to area.

\[ J = \frac{I}{A} \]  

(20)

If an electric field \( E \) is applied to the material, an electric current will flow whose density will be given by

\[ J = \sigma E \]  

(21)

Where \( \sigma \) is called the electrical conductivity of the material (discussed in the previous paragraph). The reciprocal of conductivity is known as electrical resistivity \( \rho \). For a rectangular shaped sample as shown in the figure 15, the resistance \( R \) is given as

\[ R = \rho \frac{l}{wt} \]  

(22)

Where \( l \) is the length, \( w \) is the width and \( t \) is the thickness of the sample.

Figure 15. Sample Dimensions for Definition of Sheet Resistance.
When length and breadth are equal, that is \( l = w \), the resistance of the sample becomes

\[
R = \frac{\rho}{t} = \text{Sheet resistance} \tag{23}
\]

The quantity sheet resistance is the resistance of one square of the film and independent of the size of the square. The sheet resistance is expressed as ohms/square.

The most commonly used method to find the sheet resistance is a four point probe technique, first proposed by L.B. Valdes in 1954[6]. A typical schematic set up is shown in Figure 16.

![Figure 16. Schematic of the Four Point Probe Set Up.](image)

When the probes are placed on a material of semi infinite volume, the resistivity is given by

\[
\rho = \frac{V2\pi}{I} \left[ \frac{1}{d_1} + \frac{1}{d_2} - \frac{1}{d_1 + d_2} - \frac{1}{d_2 + d_3} \right] \tag{24}
\]

When the probes are equispaced, that is \( d_1 = d_2 = d_3 = d \), then

\[
\rho = \frac{V2\pi d}{I} \tag{25}
\]

If the material is in the form of an infinitely thin film resting on an insulating support, then
\[ \rho = \left( \frac{V}{I} \right) \frac{\pi}{\ln 2} \]  \hspace{1cm} (26)

\( \pi/\ln 2 \) is the correction factor. So if the thickness of the film were known, the resistivity of the film can be calculated by calculating the sheet resistance of the film using a simple four probe set up, using the following equation

\[ R_{\text{sheet}} = 4.532 \left( \frac{V}{I} \right) \]  \hspace{1cm} (27)

where the correction factor \( \pi/\ln 2 = 4.532 \) and subsequently multiplying sheet resistance with the thickness of the film, since

\[ \rho = R_{\text{sheet}} t \]  \hspace{1cm} (28)

Under the influence of an electric field, the electrons begin to move in a specific direction and such directional motion is termed drift. The average velocity of this motion is known as the drift velocity \( V_d \).

If \( N \) is the number density of electrons, the current density is given by

\[ J = N e V_d \]  \hspace{1cm} (29)

where \( e \) is the electron charge.

Combining equations (21) and (29)

\[ V_d = \left\{ \frac{\sigma}{N e} \right\} E \]  \hspace{1cm} (30)

In the above equation the proportionality factor is called Mobility \( \mu \) of charge carriers.

\[ \mu = \frac{\sigma}{N e} \]  \hspace{1cm} (31)

The charge carrier mobility is related to the effective mass of the charge carriers \((m^*)\) and the relaxation time \((\tau)\) according to

\[ \mu = \frac{e \tau}{m^*} \]  \hspace{1cm} (32)

In order to determine the conductivity type of the sample (whether the sample is n-type or p-type), Hall Effect measurement is performed. It also allows determination of density of charge carriers and their mobility values.

When a current is passed through a slab of material in the presence of a transverse magnetic field, a small potential difference, known as the hall voltage, is developed (between face 1 and face 2), in a direction perpendicular to both the current
and the magnetic field. Face 1 is positive for p-type samples, whereas it is negative for n-type samples, mathematically it is given by

\[ V_H = R_H I(B/t) \]  

(33)

**Figure 17. The Hall Effect Phenomenon.**

where \( V_H \) is the Hall voltage, \( B \) is the magnetic field and \( I \) is the current through the sample. \( R_H \) is the Hall coefficient and is related to the carrier density according to the relation

\[ R_H = r_H (1/Ne) \]  

(34)

where \( r_H \) is the Hall scattering factor. The value of it depends on the geometry of the scattering surface and the mechanisms by which the carriers are scattered. In general, it does not vary significantly from unity.

For n-type semiconductors, \( R_H \) is negative, while for p-type it is positive. Hall effect measurements in conjunction with the measurement of conductivity, enable the calculation of the mobility of charge carriers [6].

From equations (31) and (34)

Mobility \( \mu = R_H \sigma \)  

(35)

**2.2 Electrical Conduction in Polycrystalline Thin Films**

In polycrystalline thin films, the conduction mechanism is dominated by the inherent inter crystalline boundaries (grain boundaries) rather than intra crystalline characteristics. These boundaries generally contain fairly high densities of interface states which trap free carriers from the bulk of the grain and scatter free carriers by virtue of inherent disorders and the presence of trapped charges. The interface states result in a space charge region in the grain boundaries. Due to this space charge region, band bending occurs resulting in potential barriers to charge transport. The most commonly
used model to explain the transport phenomenon in poly crystalline films is the Petritz model. According to this model, the current density is given by the relation

\[
J = e \mu_o n \exp \left( -\frac{e \phi_{gb}}{kT} \right) E
\]  

(36)

Where \( \mu_o = (M/n_c kT) \), \( \phi_{gb} \) is the height of the potential barrier, \( n_c \) is the number of crystallites per unit length along the film, and \( M \) is a factor that is barrier dependent.

The grain boundary potential barrier \( \phi_{gb} \) is related to \( N_g \) and \( N_{gb} \), the number of carriers in the grain and the grain boundary, respectively by

\[
\phi_{gb} = kT \ln \left( \frac{N_g}{N_{gb}} \right)
\]

(37)

The prefactor in the (36) is the conductivity of the charge carriers dominated by grain boundaries \( \sigma_g \).

Thus the grain boundary limited mobility can be written as

\[
\mu = \mu_o \exp \left( -\frac{e \phi_b}{kT} \right)
\]

(38)

An alternative equation for \( \mu_g \) is

\[
\mu_g = e l^* (2\pi m^* kT)^{-\frac{1}{2}} \exp \left( -\frac{e \phi_b}{kT} \right)
\]

(39)

Where \( l^* \) is the average width of the grains. In order that conduction of any sort takes place a certain amount of energy needs to be given to the system, which is called conductivity activation energy \( E_\sigma \).

\[
E_\sigma = E_a + e \phi_{gb}
\]

where \( E_a \) is the carrier activation energy.

2.3 TCOs in General

As discussed in the previous section electrical conductivity \( \sigma \) depends on the concentration \((N)\) and mobility \( \mu \) of relevant free carrier. In order to obtain films with high conductivity, high carrier concentration and mobility should be simultaneously realized. The electrical properties of the oxides depend critically upon the oxidation state of the metal component, stoichiometry of the oxide and on the nature and quantity of impurities incorporated in the films, either intentionally or unintentionally.
Stoichiometric oxides are insulators, i.e., ZnO, SnO₂, In₂O₃, etc, due to their large band gaps. They can be made highly conductive by doping (incorporation of impurity). For example, in ZnO, Zinc atom contributes two electrons to the formation of the bond with oxygen. When ZnO is aluminum doped, aluminum replaces some of the Zinc. But when oxidized aluminum provides three electrons, one more than Zinc, this electron would disrupt the electro static distribution of the lattice; this electron is not “free” to appreciably move about the lattice. It is unstable and can be easily elevated to the conduction band with the external application of energy.

The most commonly used TCOs SnO₂ and In₂O₃ are doped with Fluorine and Tin respectively. Fluorine doping gives superior performance compared with metallic dopants, in TCOs. A theoretical understanding of this advantage of fluorine can be obtained by considering that the conduction band of oxide semiconductors is derived mainly from metal orbitals. If a metal dopant is used, it is electrically active when it substitutes for the primary metal (such as zinc or tin). The conduction band thus receives a strong perturbation from each metal dopant, the scattering of conduction electrons is enhanced, and the mobility and conductivity are decreased. In contrast, when fluorine substitutes for oxygen, the electronic perturbation is largely confined to the filled valence band, and the scattering of conduction electrons is minimized [7]. Doping essentially increases conductivity by increasing carrier concentration but very high doping would lead to a decrease in mobility due to various scattering mechanisms like ionized impurity scattering, neutral impurity scattering etc. The conduction in heavily doped polycrystalline thin films is largely limited by dominant scattering mechanisms in addition to grain boundaries.

Additionally, introduction of point defects or oxygen vacancies in the lattice of the oxides can increase the conductivity of a TCO. In an oxide, oxygen vacancies produce donor sites. This is done by the reduction of the cation to which the oxygen atoms were bound, thus creating a dangling bond—an electron pair. These electrons, upon receipt of a specific amount of energy (the activation energy for the defect) can enter the conduction band.
The oxygen vacancies act as doubly ionized donors and contribute at a maximum two electrons to the electrical conductivity as shown in the following equation:

\[ \text{O}_\text{O} \rightarrow 0.5 \text{O}_2(\text{g}) + \text{V}_\text{O}^{**} \]  

(40)

Where \( \text{O}_\text{O} \) represents bonded oxygen; \( \text{V}_\text{O} \) represents an oxygen vacancy with \( ** \) being the electron pair.

TCOs can have oxygen vacancies introduced in two ways. The first is by synthesizing the material with a deficiency of \( \text{O}_2 \) as one of the reactants or having a reducing ambient while synthesizing. Alternatively, the compound can be subjected to a reducing post synthetic ambient, such as \( \text{H}_2 \), often at elevated temperatures.

Ternary TCOs like \((\text{Zn}_2\text{SnO}_4, \text{Cd}_2\text{SnO}_4, \text{and CdIn}_2\text{O}_4)\) have intrinsic n-type conductivity due to a process of self doping by forcing one cation to assume the lattice site of the other cation type. For example in the inverse spinel structure of \( \text{Cd}_2\text{SnO}_4 \), half of the \( \text{Cd} \) occupies the tetrahedral sites and the other half occupies the octahedral sites, whereas \( \text{Sn} \) occupies only octahedral sites. The oxygen is fourfold coordinated. Some of the \( \text{Sn} \) atoms replace the cadmium atoms in the octahedral sites, termed as \( \text{Sn on cadmium anti site} \). Due to the two extra electrons of \( \text{Sn} \), the lattice is disturbed leading to intrinsic n-type conductivity [8]. The Electronic properties of the materials will be discussed in the next chapter.
CHAPTER 3
MATERIAL PROPERTIES AND LITERATURE REVIEW

3.1 Electronic Properties of SnO₂ and ITO

Due to excellent optical and electrical properties, SnO₂ is the most commonly used TCO for CdTe solar cells. SnO₂ is an n-type, wide-band-gap semiconductor with the tetragonal rutile (TiO₂) structure. The electrical conductivity of SnO₂ results primarily from the existence of oxygen vacancies, which act as donors. The Sn atoms are on a body centered tetragonal lattice and oxygen atoms in a hexagonal closed packed structure as shown in figure 18 [9,10].

![Figure 18. Structure of Tin Oxide.](image)

Commercially available SnO₂ thin films typically are deposited by atmospheric pressure chemical-vapor deposition (APCVD) using tin tetrachloride (TTC). Researchers have demonstrated higher-quality film results when TTC is replaced with tetramethyltin (TMT). The temperature window for SnO₂ film growth is between 500° and 700°C. The film is well crystallized at 500°C. Intrinsic SnO₂ films are randomly oriented, whereas F-doped films exhibit a strong (200) preferred orientation.
As the growth temperature increases, grain size increase, hence surface roughness also increases. Without F-doping, the film resistivity is $\sim 1 \Omega$-cm. With F-doping, the film resistivity is $\sim 5 \times 10^{-4}$ $\Omega$-cm.

Fluorine doping not only increases the carrier concentration, but also increases the electron mobility ($\mu$) of the film. This observation is contrary to what is expected from ionized impurity scattering. For undoped SnO$_2$ films, $\mu$ is $\sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and electron concentration is in the low-$10^{18}$ cm$^{-3}$ range. Assuming O$_2$ vacancies are dominant donors in undoped SnO$_2$, and each oxygen vacancy contributes two electrons to SnO$_2$, for a carrier concentration of low $10^{18}$ cm$^{-3}$, the oxygen vacancy concentration should be about high-$10^{17}$ cm$^{-3}$. For F doped SnO$_2$ films, the electron concentration increases to mid-$10^{20}$ cm$^{-3}$, which indicates the F ion concentration should also be mid-$10^{20}$ cm$^{-3}$. Although the ion concentration increases significantly for F doping, the $\mu$ does not decrease, but increases from $\sim 1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to 40 cm$^2\text{V}^{-1}\text{s}^{-1}$. This observation indicates that the ion scattering is not a dominant scattering mechanism for SnO$_2$: F film. Grain boundary contribution to the film resistivity is negligibly small for the films with thickness above 350 nm and carrier concentration above $2 \times 10^{20}$ cm$^{-3}$. Generally, for SnO$_2$ films that are $\sim 1$ $\mu$m thick, the average transmission is $>80\%$ in the visible spectral range. F-doped films have higher absorption than the undoped films. For undoped SnO$_2$ films, the optical absorption (average between 500 and 900nm) is $\sim 600 \text{ cm}^{-1}$ compared to $\sim 1200 \text{ cm}^{-1}$ for F-doped film [11].

In$_2$O$_3$ is an n-type transparent conductive oxide crystallizes in the cubic bixbyte structure, which is similar to the fluorite structure, but one fourth of the anions are vacant allowing for small shifts of the ions. In$_2$O$_3$ has two non-equivalent six-fold coordinated cation sites. Figure 18 shows the two cation sites, which are referred to as equipoints "b" and "d". The b site cations have six equidistant oxygen anion neighbors, which lie approximately at the corners of a cube with two anion structural vacancies along one body diagonal. The d site cations are coordinated to six oxygen anions at three different distances, which lie near the corners of a distorted cube with two empty anions along one face diagonal [19].
As prepared, In$_2$O$_3$ generally lacks stoichiometry due to oxygen-array vacancies. At high O$_2$ vacancies, a vacancy band forms and overlaps $E_c$ at the bottom of the conduction band producing a degenerate semiconductor. The O$_2$ vacancies act as doubly ionized donors and contribute at a maximum two electrons to the electrical conductivity [17].

Indium Tin Oxide is essentially formed by substitututional doping of In$_2$O$_3$ with Sn which replaces the In$^{3+}$ atoms from the cubic bixbyte structure of In$_2$O$_3$. Tin acts as a cationic dopant in the In$_2$O$_3$ lattice and substitutes the indium. In In$_2$O$_3$, since indium has a valence of three, the tin doping results in $n$ doping of the lattice by providing an electron to the conduction band. The ITO films are extremely conductive and conductivities as low as 1.5 $\times$ 10$^{-4}$ $\Omega$-cm have been achieved for carrier concentrations of the order of 10$^{21}$ cm$^{-3}$. The average transmittance in the visible spectrum ranges from 85% to 90%. The band gap of ITO has a wide range from 3.6 eV to 4.0eV. It is important to note that at high dopant concentrations, the observed carrier concentration of ITO films is lower than that expected assuming that every soluble tin atom contributes one free electron. This implies that a portion of the tin remains electrically inactive.

According to the Frank and Kostlin model, formation of the following two neutral defects compensates for the Sn donor. Two Sn$^{4+}$ ions which are not on nearest neighbor positions loosely bound to an interstitial oxygen anion. This interstitial defect dissociates on annealing under reducing conditions( Sn$_2$Oi$^\prime\prime\rightarrow2$Sn$+2e+1/2$O$_2$(g)).The tin pair substituting two neighboring indium atoms strongly binds additional oxygen, forming a neutral complex which consists of the two Sn$^{4+}$ and the additional oxygen, that is, Sn$_2$O$_4$[17].

![Figure 19. Structure of ITO.](image-url)
The mobility of ITO films decreases as carrier concentration increases due to scattering by neutral and ionized impurity scattering, with ionized impurity scattering dominating.

3.2 The Effect of SnO2 and ITO Front Contacts on CdS/CdTe Solar Cells

Thin film CdS/CdTe solar cells fabricated on SnO2-coated glass have been found to have higher efficiencies than similar cells produced on indium–tin oxide (ITO) coated glass substrates. Further investigation implicated the CdS/ITO interface as the cause of the problem; current-voltage measurements revealed that on heating in air the CdS/ITO junction became rectifying. This is consistent with recently reported findings which show that the work function of ITO is raised above that of CdS by oxidative treatments (such as heating in air) which would make the ITO/CdS junction rectifying rather than ohmic.

The cells used for study were fabricated in an identical fashion. The basic structure of all three cells was the same: ~200 nm CdS deposited by physical vapor deposition (PVD) onto the TCO (SnO2 and ITO), followed by ~5.5 µm CdTe deposited by close spaced sublimation at source and substrate temperatures of 600 ºC and 500 ºC respectively. The cells were then treated with CdCl2 (known to improve the performance significantly by depositing ~150 nm CdCl2 by PVD and then heated in air at 400 ºC for 30 min in the case of a) SnO2 b) ITO30 and 15 min in the case of ITO15. After thorough rinsing in water to remove any remaining CdCl2, they were etched in 0.03% Br–methanol for 10 to 15 seconds before gold contacts were deposited.

The figure 20 shows the photovoltaic output characteristics of three cells measured under AM1.5 illumination at room temperature. The characteristics labeled ITO30 and ITO15 were recorded from cells formed on indium–tin oxide coated glass; that labeled SnO2 was from a cell on tin oxide coated glass. Clearly the superiority of SnO2 as TCO is evident. The photovoltaic parameters (short circuit current density, Jsc, open circuit voltage, Voc, fill factor, FF, and conversion efficiency, η, series resistance, R_s, and shunt resistance, R_sh) of the three cells are listed in table 2.
Figure 20. The J-V Characteristics of SnO\(_2\), ITO Cells.

Table 2. Photovoltaic Parameters of SnO\(_2\) and ITO CdS/CdTe Solar Cells.

<table>
<thead>
<tr>
<th>TCO</th>
<th>Sheet R[Ω/sq]</th>
<th>(V_{oc}) [mV]</th>
<th>(J_{sc}) [mA/cm(^2)]</th>
<th>FF[%]</th>
<th>η[%]</th>
<th>(R_s[Ω\text{-cm}^2])</th>
<th>(R_{sh}[Ω\text{-cm}^2])</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO(_2)</td>
<td>17</td>
<td>684</td>
<td>27.3</td>
<td>54.4</td>
<td>10.1</td>
<td>6</td>
<td>196</td>
</tr>
<tr>
<td>ITO15</td>
<td>7</td>
<td>714</td>
<td>22.6</td>
<td>44.9</td>
<td>7.3</td>
<td>54.1</td>
<td>171</td>
</tr>
<tr>
<td>ITO30</td>
<td>7</td>
<td>623</td>
<td>20.2</td>
<td>36.7</td>
<td>4.6</td>
<td>34</td>
<td>82</td>
</tr>
</tbody>
</table>

The saturation of IV characteristics of ITO cells for \(V > V_{oc}\) suggests the presence of some kind of additional series diode component such a rectifying barrier at one of the contacts. Generally this barrier is assumed to be at the back contact since the electron affinity of CdTe is approximately 4.5 eV and the distance between the conduction band and the fermi level, in the case of p-CdTe, can be estimated to be 1.38-1.45 eV. Thus the value of the work function of CdTe is about 5.9eV. Due to this high work function of CdTe (\(\phi=5.9\) eV), it is very difficult to avoid the formation of a Schottky contact. Typically CdTe contacts are mostly tunneling. But from the IV characteristics it can be inferred that any such barrier could be present at the CdS/TCO interface since all the cells have the same back contact and the fact that the characteristics
of the cells become worse with increase in annealing times after the CdCl₂ deposition, indicates that the effect may be associated with heating. To investigate the effects of heating on the TCO/CdS interface, a number of SnO₂/CdS/In and ITO/CdS/In samples were prepared. Indium was used as the back contact as it is known to make a good ohmic contact to CdS. Room temperature current-voltage (IV) characteristics were measured in the dark for both as-deposited devices and after heating in air for 30 min at 400 °C, i.e. mimicking the CdCl₂ treatment. The results are shown in figure 21. (The saturation at approximately ± 3.8 mA was a consequence of the current limit on the instrumentation.).

Figure 21. The Dark IV Characteristics of SnO₂/CdS/In in the Forward and Reverse bias (a) Before Annealing (b) After Annealing.

In the figure above the dark IV characteristics of SnO₂/CdS/In in the forward and reverse bias, before annealing (a) and after annealing(b), indicate that the SnO₂/CdS contact was ohmic and remained ohmic even after annealing, with an exception of a small increase in series resistance from 0.62 to 1.3Ωcm². This suggests that any
interaction between the CdS and SnO$_2$ was probably of minimal significance for the performance of the cell.

**Figure 22. The Dark IV Characteristics of ITO/CdS/In in the Forward and Reverse bias (a) Before Annealing (b) After Annealing.**

In figure 22, the dark I-V characteristics of ITO/CdS/In in the forward and reverse bias before annealing (a) and after annealing (b) indicates that the ITO/CDS interface does not remain ohmic but becomes rectifying after annealing. Assuming that the contact between the In and CdS layer was ohmic, since that was common to both the SnO$_2$/CdS/In and the ITO/CdS/In devices, then the rectifying effect which appeared after heating of the samples would seem to be due to the contact between the ITO and CdS.
Hence, annealing the CdS/ITO interface for 30 min at 400 °C in air, as used in the CdCl$_2$ treatment clearly resulted in some interaction, which impeded the flow of charge.

![Graphs showing the Dark IV Characteristics of ITO/CdS/In at Different Lengths of Annealing Times.](image)

Figure 23. The Dark IV Characteristics of ITO/CdS/In at Different Lengths of Annealing Times.

To determine at what time of annealing does the interface becomes rectifying, the dark IVs of ITO/CdS/In at different annealing times of 10, 20 and 30 minutes were measured and the results obtained are shown in figure 23. It is clear from the figure above that the ITO/CdS interface started to become rectifying within 10 minutes heating time at 400 °C, and had become fully rectifying after ~20 minutes.

Since In is a donor impurity in CdS, cross diffusion of In from the ITO into the CdS would act to increase its conductivity.
Generally, this might be expected to improve the injection of carriers across the ITO/CdS interface, reducing the contact resistance and rendering the contact even more ohmic, i.e. the reverse of what was observed. Another recent study of the oxidative-reductive behavior of ITO surfaces using x-ray (XPS) and ultraviolet (UPS) photoelectron spectroscopy has indicated that the work function is dependent on the surface oxygen concentration. In particular, the UPS measured work function of as-received ITO was found to be low (~ 4 eV) as a consequence of adventitious contamination, but increased substantially (5 eV) following various surface treatments. Importantly, oxidative treatments raised the work function of the surface [21]. The annealing treatments carried out in the present study were all undertaken in air and, assuming that oxygen was able to diffuse through the thin CdS layer, may be presumed to be oxidative. In that case, the UPS studies would imply an increase in the work function. However, since CdS is a n-type semiconductor, contact materials should have a low work function, ideally less than the electron affinity if they are to be injecting. The electron affinity of CdS is 4.5 eV, greater than as-received ITO, but less than fully oxidized (i.e. heat treated) ITO. The implication is that the heat treatment changes the ITO from an injecting (ohmic) to a rectifying (Schottky barrier) contact by raising the ITO work function through surface oxidation. The observations presented here strongly suggest that ITO is not well suited to use in CdS/CdTe thin film solar cells. Although the sheet resistance of ITO coated glass is generally less than corresponding SnO2 coated glass, ITO is not as stable to subsequent processing steps as SnO2. Moreover, it would appear that in its ‘clean’ state, i.e. the more controlled surface, the high work function of ITO makes it unsuitable in principle as an ohmic contact to n-CdS [20].

3.3 Properties of Cd₂SnO₄ and Zn₂SnO₄

The spinel structure has the form of AB₂O₄, where A is a metal ion with a +2 valence and B is a metal ion with a +3 valence or +4 valency. This structure is viewed as a combination of the rock salt and zinc-blend structures. The oxygen ions are in face-centered cubic close packing. A and B ions occupy tetrahedral and octahedral interstitial sites.
Spinel structure can be divided into two types: normal and inverse spinel. In normal spinels, A\(^{2+}\) ions are on tetrahedral sites and the B\(^{3+}\) (or higher example B\(^{4+}\)) ions are on octahedral sites. In inverse spinels, the A\(^{2+}\) ions and half the B\(^{3+}\) ions are on octahedral sites; the other half of the B\(^{3+}\) are on tetrahedral sites, B(AB)O\(_4\) as shown in figure 24 [22,23].

Cd\(_2\)SnO\(_4\) (CTO), Zn\(_2\)SnO\(_4\) (ZTO) are TCOs with inverse spinel structure with exceptional electrical and optical properties. Zn\(_2\)SnO\(_4\) (ZTO) (inverse spinel), is superior to CTO in optical properties but has poor electrical properties. By optimizing the sputtering method and pot annealing conditions of CTO films, electron mobilities as high as 65 cm\(^2\) V\(^{-1}\) s\(^{-1}\) have been achieved for a carrier concentration of 2\(\times\)10\(^{20}\) cm\(^{-3}\).

Even at a high carrier concentration of ~9\(\times\)10\(^{20}\) cm\(^{-3}\), mobilities as high as 55 cm\(^2\) V\(^{-1}\) s\(^{-1}\) have been observed. These mobilities are 2-3 times higher than those of commercial SnO\(_2\) films doped to similar levels.
Free carriers in CTO films are thought to result from oxygen deficiencies in the film accommodated either as oxygen vacancies or cadmium interstitials or a combination of both. This results in resistivities as low as $1.3 \times 10^{-4}$ $\Omega \cdot \text{cm}$.

![Figure 25. Transmission and Absorbance Spectra of CTO and SnO$_2$ Thin Films.](image)

This is almost seven times lower than conventional TTC based SnO$_2$ films and about 2.5 times lower than TMT based SnO$_2$ films with resistivities of $\sim 3.3 \times 10^{-4}$ $\Omega \cdot \text{cm}$. Cd$_2$SnO$_4$ films have significantly better optical properties than conventional SnO$_2$ films. The absorbance of the CTO film, in the visible range, is much smaller than that of the SnO$_2$ film of the same sheet resistance. For example, at 600 nm, the absorbance of the CTO film is only 0.6%, compared to 12.2% of the SnO$_2$ film. This appears to be due to the high electron mobility of CTO films.

![Figure 26. Relationship Between $J_{sc}$ and Transmission of SnO$_2$ and CTO Films.](image)
In CdTe cells replacing the 10000 Å SnO\textsubscript{2} film with a 2500 Å CTO film yielded an increase in J\textsubscript{sc} of more than 1.5 mA/cm\textsuperscript{2}. Zn\textsubscript{2}SnO\textsubscript{4} has better optical properties than CTO but low electrical conductivity and mobility due to its structure [12]. Polycrystalline ZTO thin films form in the inverse spinel crystal structure. However, the spinel lattice is locally distorted enough to form two distinct octahedrally coordinated Sn and Zn sites. The disorder in the Sn and Zn sites in the lattice significantly limits the mobility of the carriers, possibly by disrupting the edge-sharing nature of the octahedrally coordinated cations [14].

Single-phase, spinel zinc stannate (Zn\textsubscript{2}SnO\textsubscript{4}) thin films were grown by rf magnetron sputtering onto glass substrates. The as deposited films were amorphous but subsequent annealing at 600º C gave polycrystalline uniaxially oriented films with resistivities of 10\textsuperscript{-2}-10\textsuperscript{-3} Ω-cm, mobilities of 16–26 cm\textsuperscript{2}/V s, and n-type carrier concentrations in the low 10\textsuperscript{19} cm\textsuperscript{3} range were achieved. X-ray diffraction peak intensity studies established the films to be in the inverse spinel configuration. A pronounced Burstein–Moss shift moved the optical band gap from 3.35 to as high as 3.89 eV. Figure 27 shows transmittance, reflectance, and absorptance for wavelengths between 300 and 2500 nm for a ZTO film. The absorptance is less than 1.5% over the visible spectrum. The slight rise in the absorptance curve near 2300 nm is due to the onset of absorption by free electrons in the conduction band [13]. Figure 28 gives the shift in the band gap of ZTO films with increase in carrier concentration.

![Figure 27. Transmittance, Reflectance, and Absorption for Wavelengths Between 300 and 2500 nm for a ZTO Film.](image)
3.4 The Effect of Cd₂SnO₄ and Zn₂SnO₄ on CdS/CdTe Solar Cells

The solar cell structure that was used to find the effect of both CTO and ZTO layers is as follows.

![Figure 29. The Structure of CdS/CdTe Solar Cell to Find the Effect of Both CTO and ZTO Layers is as Follows.](image)

In this study, it was found that the interdiffusion of the CdS and Zn₂SnO₄ ~ZTO layers can occur either at high temperature (550–650 °C) in Ar or at lower temperature (400–420 °C) in a CdCl₂ atmosphere. By integrating a Zn₂SnO₄ film into a CdS/CdTe solar cell as a buffer layer, this interdiffusion feature can solve several critical issues and improve device performance and reproducibility of both SnO₂-based and Cd₂SnO₄-based CdTe cells.
Interdiffusion consumes the CdS film from both the ZTO and CdTe sides during the device fabrication process and improves quantum efficiency at short wavelengths. The ZTO film acts as a Zn source to alloy with the CdS film, which results in increases in the band gap of the window layer and in short-circuit current density Jsc. Interdiffusion can also significantly improve device adhesion after CdCl₂ treatment, thus providing much greater process latitude when optimizing the CdCl₂ process step. The optimum CdCl₂-treated CdTe device has high quantum efficiency at long wavelength, because of its good junction properties and well-passivated CdTe film.

![Figure 30. Relative Quantum Efficiencies of CTO/CdS/CdTe Solar Cell and CTO/ZTO/CdS/CdTe Solar Cells.](image)

The figure above gives the relative quantum efficiencies of CTO/CdS/CdTe solar cell and CTO/ZTO/CdS/CdTe solar cells. The table below gives a summary of the parameters of the solar cell with different TCOs [16].

**Table 3. Summary of the Parameters of the Solar Cell with Different TCOs [16].**

<table>
<thead>
<tr>
<th>Device structure</th>
<th>( V_{oc} ) [mV]</th>
<th>( J_{sc} ) [mA/cm²]</th>
<th>FF[%]</th>
<th>( \eta )[%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂/CdS/CdTe</td>
<td>806.7</td>
<td>22.61</td>
<td>74.02</td>
<td>13.5</td>
</tr>
<tr>
<td>CTO/CdS/CdTe</td>
<td>805.2</td>
<td>23.53</td>
<td>73.77</td>
<td>14.0</td>
</tr>
<tr>
<td>SnO₂/ZTO/CdS/CdTe</td>
<td>830.1</td>
<td>24.10</td>
<td>74.15</td>
<td>14.8</td>
</tr>
<tr>
<td>CTO/ZTO/CdS/CdTe</td>
<td>844.3</td>
<td>25.00</td>
<td>74.82</td>
<td>15.8</td>
</tr>
</tbody>
</table>
The highest efficiency for CdTe solar cell was achieved by NREL by reduction of photocurrent loss in the TCO (by using CTO, reduced the loss in $J_{sc}$ to 0.62 mA/cm$^2$), reduction of photocurrent loss in CdS (by using ZTO from which interdiffusion of Zn occurs and CdS gets consumed from both ends, reduced $J_{sc}$ loss to 1 to 1.3 mA/cm$^2$) and photocurrent loss in recombination centers in CdTe (by optimizing the CdCl$_2$ treatment with the help of ZTO film, up to 0.5 mA/cm$^2$). The table below gives the $J_{sc}$ losses in different TCOs [15].

**Table 4. $J_{sc}$ Losses in Different TCOs.**

<table>
<thead>
<tr>
<th>TCO</th>
<th>$R_n$(Ω/sq)</th>
<th>$J_{sc}$ loss due to TCO absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$ (TTC)</td>
<td>8-10</td>
<td>2.8</td>
</tr>
<tr>
<td>SnO$_2$(TMT)</td>
<td>7-8</td>
<td>1.3</td>
</tr>
<tr>
<td>CTO</td>
<td>7-8</td>
<td>0.62</td>
</tr>
<tr>
<td>CTO/ZTO</td>
<td>7-8/~10$^5$-10$^6$</td>
<td>0.68</td>
</tr>
</tbody>
</table>

The parameters of the highest efficiency CTO/ZTO/CdS/CdTe solar cell achieved by NREL are as follows.

**Table 5. The Parameters of Highest Efficiency CTO/ZTO/CdS/CdTe Solar Cell.**

<table>
<thead>
<tr>
<th>Cell#</th>
<th>$V_{oc}$ [mV]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>FF [%]</th>
<th>$\eta$ [%]</th>
<th>Area (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W547-A</td>
<td>847.5</td>
<td>25.86</td>
<td>74.45</td>
<td>16.4</td>
<td>1.131</td>
</tr>
<tr>
<td>W567-A</td>
<td>845.0</td>
<td>25.88</td>
<td>75.51</td>
<td>16.5</td>
<td>1.032</td>
</tr>
</tbody>
</table>
CHAPTER 4
EXPERIMENTAL METHODS

4.1 Material Deposition

4.1.1 Chemical Vapor Deposition Process

The substrates used were Corning 7059 borosilicate glass (1.25” X 1.45” X 0.032”). These substrates were cleaned in a 10% by volume HF solution followed by a thorough rinse in deionized water. They were subsequently dried with compressed nitrogen.

Primarily SnO₂ was deposited on the substrates by chemical vapor deposition technique. The reactor consisted of a quartz tube which was heated by RF coils to above 450°C. The organometallic tin source used was TMT (Tetra Methyl Tin) and ultra high purity Helium was used as the carrier gas, and Oxygen served as the oxygen source. The Fluorine dopant used was the halocarbon 13B1. The SnO₂ was deposited in a bilayer form for the standard cell, the first layer being Fluorine doped and the next layer being intrinsic. All the gases are introduced into the reactor via MFC (Mass Flow Controller). The oxidation reduction chemical reaction for this process is as follows.

\[
\text{Sn(CH}_3\text{)}_4 \text{(Vap)} + 14\text{O}_2 (\text{gas}) \rightarrow \text{SnO}_2 (\text{solid}) + 4\text{CO}_2 (\text{gas}) + 6\text{H}_2\text{O (gas)}
\] (41)

A simplified schematic of the deposition system is presented below.

Figure 31. Simplified Schematic of MOCVD Set-up.
4.1.2 Sputtering

SnO₂ was also deposited by RF magnetron sputtering. SnO₂ was reactivity sputtered from a 99.99% pure Sn (metal) target in 25% O₂ in an Argon environment. In₂O₃ was also reactivity sputtered from 99.99% pure Indium target in 25% O₂ in Argon. Indium Oxide doped with Tin (ITO) was sputtered from a 90% In₂O₃:10% SnO₂, ITO target in pure Argon.

Cadmium stannate was co-sputtered from 99.999% pure CdO and SnO₂ targets. Cadmium Indium Oxide was co-sputtered reactivity from a Cd and In metallic targets (99.999%) in 25% O₂ with Argon. Zinc stannate was prepared by co-sputtering from ZnO and SnO₂ (99.99%) targets.

The vacuum chamber was a Consolidated Vacuum Corp. model; the sputtering guns were Kurt J. Lesker Torus TRS3FSA models; and Advanced Energy RFX-600 power supplies supplied the RF power. The sputtering sources were positioned such that the center line of each source created an angle of approximately forty degrees with respect to a plane parallel to the substrate holder. The substrate holder was rotated to ensure uniform film thickness.

The total pressure in the chamber was maintained at 3.0 mT in all cases. Before each deposition, the chamber was pumped down to a background pressure of approximately in the low 10⁻⁶ Torr range.

![Figure 32. Position of Sputtering Sources and Substrate Holder.](image-url)
Annealing experiments were carried out in a simple quartz tube which has a vacuum outlet and gas inlet in which the samples were placed on graphite holders and heated by two halogen lamps (1000 W) - one on top and one at the bottom. The films were mostly annealed in He ambient, however O₂ and H₂ were also available to carry out oxidizing and reducing experiments respectively if necessary.

**4.1.3 Chemical Bath Deposition Process**

The CdS window layer used in this thesis is deposited by a process called Chemical Bath Deposition (CBD). The Cadmium source was Cadmium acetate and Thiourea was used as the sulphur source. Ammonium hydroxide, a base and ammonium acetate, which served as a buffer, were also used, all combined in a solution of 600ml of H₂O held in a double jacketed beaker with a capacity of 1000 ml. At specific time intervals measured volumes of the thiourea and Cadmium acetate precursors were added to the solution, which was maintained at a constant temperature of 85°C by circulating heated ethylene glycol through the walls of the double jacketed beaker. (The set up is illustrated in figure 33). A proposed mechanism for the reactions was given by J. Herrero et al [24]:

\[
\text{Cd(CH}_3\text{COO)}_2 \leftrightarrow \text{Cd}^{2+} + 2\text{CH}_3\text{COO}^- \\
\text{NH}_3 + \text{HOH} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \\
\text{Cd(NH}_3)_4^{2+} + 2\text{OH}^- \leftrightarrow [\text{Cd(OH)}_2(\text{NH}_3)_2] + 2\text{NH}_3 \\
[\text{Cd(OH)}_2(\text{NH}_3)_2] + \text{SC(NH}_2)_2 \rightarrow [\text{Cd(OH)}_2(\text{NH}_3)_2\text{SC(NH}_2)_2] \\
[\text{Cd(OH)}_2(\text{NH}_3)_2\text{SC(NH}_2)_2] \rightarrow \text{CdS}_6(\text{s}) + \text{CN}_3\text{H}_5 + \text{NH}_3 + 2\text{HOH}
\]

![Figure 33. The Chemical Bath Deposition Set-up.](image-url)
4.1.4 Close Spaced Sublimation Process

The CdTe absorber layer is deposited by Closed Spaced Sublimation process (CSS). In which the CdTe powder is sublimed onto a substrate with dimensions similar to that of the corning 7059 substrate, the source such prepared is placed on a graphite holder. The substrate on which the CdTe layer is to be deposited is placed on another graphite holder, on the top facing the source. The source and the substrate are separated by spacers.

The whole set-up, as described above was placed in a closed end quartz tube, that had a vacuum outlet and gas inlet (identical to that of the annealing experimental set up). Both graphite holders (of the source and the substrate) were heated by two 2000 W halogen lamps, that caused the CdTe from the source to sublime and get deposited on the substrate which is facing it, in such close proximity.

Since the source and the substrate are in close proximity to each other, this process was termed as Close Spaced Sublimation. The experimental set up is shown in the figure below.

![Figure 34. Simplified CSS Experimental Set-up.](image)

4.1.5 Evaporation

The substrates after CdTe deposition were CdCl₂ treated. 99.999% pure CdCl₂ obtained from Fischer was pressed into circular pellets of 1cm in diameter, which were then placed on a metal boat, mounted between two copper electrodes.
The samples were placed on top of a hollow cylindrical glass holder, about 15 cm above the boat. The whole set up was placed inside a bell jar. The bell jar was pumped down to $10^{-4}$ Torr, and the boat containing the CdCl$_2$ pellets was heated by passing electric current through the copper electrodes. The CdCl$_2$ was so evaporated on the substrates to about 8000 Å in thickness. Then the CdCl$_2$ treated substrates were annealed in a He/O$_2$ ambience at 390 °C for 25 minutes, after which the excess CdCl$_2$ was rinsed away by using methanol. Then the substrates were prepared for back contact application.

### 4.1.6 Graphite Paste Application

The substrates from the previous step were subjected to a bromine methanol etch for 7-10 seconds. This was done to create a tellurium rich surface. Then graphite paste doped with HgTe and Cu was painted on the etched surface with a paint brush. Then the substrates were left to dry for about 24 hours in a evacuated dessicator, after which they were annealed in He for about 20 minutes at 240°C. Then the graphite paste was smoothened and silver paste was applied on it. After the cell areas were defined by scraping, Indium metal was applied as a metallic grid on the front contact for better collection, using a soldering gun.

### 4.2 Standard Device Structure

![Diagram of Standard Device Structure](image)

**Figure 35. Standard Device Structure.**
In this thesis, the performance of SnO$_2$ and ITO as front contacts was compared, with and without a buffer layer. The use of SnO$_2$ and In$_2$O$_3$ as buffer layers was also explored. SnO$_2$ was deposited by MOCVD and sputtering and In$_2$O$_3$ and ITO were deposited only by sputtering. In all of the above mentioned devices the CdS/CdTe junction and the back contact were kept constant and the front contacts were changed. In the section of window less junctions of chapter 5, the junction between spinel TCOs and CdTe is studied without the CdS layer. The back contact however remained the same. All the spinel TCOs were deposited by sputtering.

4.3 Material Characterization

The sheet resistance of the deposited TCO films was measured by using a simple four point probe set up. Then a portion of the film was etched by HCl and Zinc and the thickness of the film was determined by measuring with a Tencor Alpha-step 200 profilometer, and the resistivity of the film was subsequently calculated.

The crystallinity and orientation of the film was determined by powder X-Ray Diffraction pattern studies. The diffractometer was a MiniFlex (VD01417) manufactured by Rigaku with CuK$_\alpha$ radiation ($\lambda = 1.540562$ nm).

The surface topography and the surface roughness of the films were studied using an Atomic Force Microscope (Nanoscope Dimension 3000). Hall mobilities, and carrier concentrations, were obtained using a Keithley 920 Series Hall Test equipment set up. This method also provided material resistivities and sheet resistances to validate values obtained using the four-point-probe.

For optical measurements, an Oriel Cornerstone monochromator (model 74100) with an integrating sphere was utilized and transmission of the TCO films at different wavelengths was measured, using a LABVIEW program specifically written for this purpose. The optical band gaps of the TCOs were also estimated from plotting square of absorption coefficient $\alpha$ (at different wavelengths) vs wavelength.

4.4 Solar Cell Measurements

Dark and light J-V data was measured using a specifically written LABVIEW program from a Keithley 2410 1100 V source meter, keeping the cell under illumination from a solar simulator and covering the cell with a black cloth respectively.
The open Circuit Voltage and Fill Factor were directly determined from the LABVIEW program. Since in this measurement the Jsc depended on the area of the devices calculated manually under a simple microscope, it was prone to error, hence the Jsc was calculated from QE of the devices measured using the same Oriel Cornerstone monochromator (model 74100), via another LABVIEW program dedicated for operating the spectral response set up. The light source was a GE 400W/120V Quartz Line lamp (model # 43707). Values for series resistance and shunt resistance were determined by methods described in chapter one under basic device physics.
CHAPTER 5
RESULTS AND DISCUSSION

In this section the properties of fluorine doped SnO₂ (SnO₂:F) deposited by MOCVD process and indium oxide doped with tin (ITO) prepared by sputtering as described in chapter 4, are discussed.

5.1 Properties of MOCVD SnO₂ Thin Films

Tin Oxide films were deposited at a temperature of 460°C by the MOCVD technique as described in chapter 4. The thickness of the films was approximately 6000 Å and the sheet resistance value was in the range of 7-10Ω/sq. The average transmission in the visible spectrum, for these films was above 90%. The films were polycrystalline with a preferred orientation of (110), as can be seen from the XRD pattern shown in figure 36. The root mean square roughness of the films was about 7.322 nm and the grain size was about 0.12μm as determined by AFM. Figure 37 shows an AFM photograph of the surface of SnO₂ film deposited at 460°C. These MOCVD SnO₂ films have been in use for several years as the standard TCO for USF CdTe solar cells.

Figure 36. XRD Pattern MOCVD SnO₂:F Film at 460° C.
5.2 Properties of Sputtered In$_2$O$_3$ Thin Films

Indium Oxide was reactively sputtered from an In target in Ar/O$_2$ mixture (25% O$_2$). The total pressure was maintained at 3.0 mT. The film was deposited at various temperatures from room temperature (RT) to 400°C. The films deposited at RT were amorphous. From the XRD patterns of the films (figure 38), it could be seen that the films started to crystallize between 200 to 300°C and at 400°C they were well crystalline, as indicated by the intensity and FWHM, with increase in the deposition temperature, the crystallinity of the films improved.

The average transmission of the films deposited at 200°C was above 92% and the average transmission of the films deposited at higher temperatures averaged 90%. This is well within the measurement errors and therefore no real effect of the deposition temperature was seen on the transmission of the films. The resistivities the films deposited at various temperatures and their average %T in the visible region is summarized in table 6. It can be seen that as the deposition temperature increased the resistivities of the films decreased, this is due to the improvement in the crystallinity of the films.
Table 6. Properties of Reactively Sputtered In$_2$O$_3$ Thin Films.

<table>
<thead>
<tr>
<th>Deposition Temperature[°C]</th>
<th>Resistivity [Ω-cm]</th>
<th>Avg %T in Visible region</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>Too high - Could not be measured</td>
<td>86.00</td>
</tr>
<tr>
<td>200</td>
<td>11.5</td>
<td>92.48</td>
</tr>
<tr>
<td>300</td>
<td>6.8</td>
<td>90.11</td>
</tr>
<tr>
<td>400</td>
<td>0.1</td>
<td>90.55</td>
</tr>
</tbody>
</table>

Figure 38. XRD Pattern of In$_2$O$_3$ Thin Films.

Figure 39. Transmission Spectra of In$_2$O$_3$ Thin Films.
From the transmission spectra and the XRD patterns, it could be seen that the amorphous films (deposited at RT and 200°C) have a similar transmission spectra and the polycrystalline films (deposited at 300°C and 400°C) group together and have a similar transmission spectra, this could be due to the differences in the refractive indices of amorphous and polycrystalline films. These differences can affect the interference fringes.

5.3 Properties of Sputtered ITO Thin Films

The ITO films were deposited at 200 and 300°C from a 99.99% ITO target, in pure Ar at a pressure of 1.2 mT. Films were also deposited in different partial pressures of O₂, but the resistivity of the resulting films increased with O₂ partial pressure (most likely due to the reduction of oxygen vacancies), so the films were deposited in pure Ar with no O₂. The sheet resistance of ITO films ranged from 9 to 11 Ω/sq, for 2000 Å thick films deposited at 300°C and for films deposited at a temperature of 200°C the sheet resistance ranged from 13 to 15 Ω/sq, for the same thickness. The average transmission of these films ranged from 88 to 90 % in the spectral region of 400 to 900 nm. Figure 41 shows a comparison of ITO with standard SnO₂.

![Total transmission of ITO and SnO₂:F](image)

**Figure 40. The Transmission Spectra of SnO₂:F and ITO.**
The film deposited at 200°C displayed essentially random orientations as seen in figure 41, there were many crystalline orientations like <222>, (the preferred orientation of In$_2$O$_3$), <211> etc and the films deposited at 300°C showed improvement in crystallinity with the preferred orientation of <400>, as indicated by the highest intensity of the <400> peak in figure 42.

Figure 41. XRD Pattern of the ITO Film Deposited at 200°C.

Figure 42. XRD Pattern of ITO Film Deposited at 300°C.
Table 7. Properties of SnO$_2$:F and ITO Films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness[Å]</th>
<th>Resistivity [Ω-cm]</th>
<th>Carrier concentration [Cm$^{-3}$]</th>
<th>Mobility [cm$^2$V$^{-1}$s$^{-1}$]</th>
<th>Avg %T (400nm to 900nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$:F(460°C)</td>
<td>5000</td>
<td>4.16X10$^{-4}$</td>
<td>3.95X10$^{20}$</td>
<td>38</td>
<td>90-92</td>
</tr>
<tr>
<td>ITO(200°C)</td>
<td>2000</td>
<td>3.08X10$^{-4}$</td>
<td>7.14X10$^{20}$</td>
<td>28</td>
<td>88-89</td>
</tr>
<tr>
<td>ITO(300°C)</td>
<td>2000</td>
<td>1.9X10$^{-4}$</td>
<td>1.02X10$^{21}$</td>
<td>32</td>
<td>89-90</td>
</tr>
</tbody>
</table>

Figure 43. AFM Photograph of ITO Deposited at 200°C (left) and 300°C (right).

The RMS roughness of the ITO was approximately 1.715 nm and 2.664nm for samples deposited at temperatures of 200 and 300°C respectively. The roughness of ITO deposited at 300°C was almost 3 times smaller than that of standard SnO$_2$. Table 7 shows the results of hall measurements done on these films. The ITO film deposited at 300°C has the lowest resistivity owing to high carrier concentration and mobility. The AFM images of the surface of ITO deposited at 200 and 300°C are shown in figure 43.
5.4 CdTe Solar Cells with SnO$_2$:F and ITO as Front Contacts

The SnO$_2$:F and ITO films whose properties were described in the previous section were used as front contacts for CdTe solar cells. The CdS window layer was deposited by chemical bath deposition, and the absorber layer CdTe was deposited by Close space sublimation, graphite paste doped with Cu and HgTe was applied as back contact, after CdCl$_2$ treatment (every step as described in chapter 5). The cell structure of these devices is shown in figure 44.

![Figure 44. Structure of CdS/CdTe Solar Cells with SnO$_2$:F, ITO as Front Contacts.](image)

Typical solar cell results of the devices are shown in table 8.

**Table 8. Device Parameters of CdS/CdTe Solar Cells with SnO$_2$:F and ITO as Front Contacts [34].**

<table>
<thead>
<tr>
<th>Front contact</th>
<th>$V_{oc}$ [mV]</th>
<th>FF [%]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{series}$ [Ω-cm$^2$]</th>
<th>$R_{shunt}$ [Ω-cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$:F</td>
<td>740</td>
<td>63</td>
<td>22.44</td>
<td>0.68</td>
<td>1660</td>
</tr>
<tr>
<td>ITO</td>
<td>770</td>
<td>60</td>
<td>22.49</td>
<td>2.3</td>
<td>1250</td>
</tr>
</tbody>
</table>

The devices exhibited low open circuit voltage and FF. It could be inferred from the I-V characteristics of ITO device (see figure 47) that a barrier to the current flow is present, due to the existence of a diode in the opposite direction to the main junction (see figure 45) either in the front or in the back contact.
Since all the devices have the same contact and yet only those with ITO as front contacts showed this anomaly repeatedly, leads to the conclusion that the barrier was formed at the ITO – CdS interface. A recent study on the influence of oxidative and reductive treatments on the surface of ITO films lead to the conclusion that the work function of ITO films strongly depended on the surface oxygen concentration, and also that oxidative treatment lead to increase in the work function of ITO films[21]. The work function of as deposited ITO film may be around 4.0 to 4.45 eV, lesser than the electron affinity of CdS (4.5 eV), assuming that the oxygen is able to diffuse through the CdS film during device fabrication (like CdTe deposition), it would increase the work function of ITO to around 5.0 eV. However, since CdS is a n-type semiconductor, contact materials should have a low work function, ideally less than the CdS electron affinity if they are to be injecting. So the ITO junction becomes rectifying due to the formation of a Schottky barrier after oxidative surface treatments.
However, it is noted here that the work function of ITO film used for this thesis is not known. It is only assumed that the heat treatment changes the ITO from an injecting (ohmic) to a rectifying (Schottky barrier) contact by raising the ITO work function through surface oxidation as concluded by S.N. Alamri et al [20].

The addition of a high resistivity SnO$_2$ layer seems to improve the device performance, most likely by affecting the ITO surface leading to a lower work function.

5.4.1 Effect of High Resistivity (intrinsic) CVD SnO$_2$ Layer

A buffer layer of SnO$_2$ was deposited on the SnO$_2$:F and ITO substrates discussed in the previous section by MOCVD in the same chamber as SnO$_2$:F, at 460°C for a thickness of about 3000 Å. The only difference being that this film was not doped. Its resistivity was approximately 0.5 to 1 Ω-cm.

The structure of these devices is as follows

![Device Structure after the Inclusion of Buffer Layer](image)

**Figure 46. Device Structure after the Inclusion of Buffer Layer.**

55
Figure 47. I-V Characteristics of SnO₂ and ITO CdS/CdTe Solar Cells with and without Intrinsic SnO₂ Layer.

Figure 48. Spectral Response of SnO₂:F CdS/CdTe Cells with and without Intrinsic SnO₂ Layer.
Figure 49. Spectral Response of ITO CdS/CdTe Cells with and without Intrinsic SnO\textsubscript{2} Layer.

The introduction of this buffer layer improved the solar cell performance considerably. The $V_{oc}$ increased approximately 60 to 80 mV and the FF 7 to 8 \%. No significant change in $J_{sc}$ was observed because $J_{sc}$ is primarily determined by CdS thickness. The shunt resistances of the devices improved by 2000 $\Omega$-cm\textsuperscript{2}. The formation of barrier at the front contact, in the case of ITO, was eliminated, as seen from the J-V data. Table 9 summarizes the performance of the devices after the inclusion of a SnO\textsubscript{2} buffer layer.

Table 9. Device Parameters of CdS/CdTe Solar Cells with SnO\textsubscript{2}:F and ITO as Front Contacts with Intrinsic SnO\textsubscript{2} Buffer Layer [34].

<table>
<thead>
<tr>
<th>Front contact</th>
<th>Buffer Layer</th>
<th>$V_{oc}$ [mV]</th>
<th>FF [%]</th>
<th>$J_{sc}$ [mA/cm\textsuperscript{2}]</th>
<th>$R_{\text{series}}$ [$\Omega$-cm\textsuperscript{2}]</th>
<th>$R_{\text{shunt}}$ [$\Omega$-cm\textsuperscript{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO\textsubscript{2}:F</td>
<td>SnO\textsubscript{2}-i</td>
<td>820</td>
<td>72</td>
<td>22.3</td>
<td>0.60</td>
<td>3300</td>
</tr>
<tr>
<td>ITO</td>
<td>SnO\textsubscript{2}-i</td>
<td>820</td>
<td>69</td>
<td>22.1</td>
<td>0.53</td>
<td>3300</td>
</tr>
</tbody>
</table>

The SnO\textsubscript{2}:F/SnO\textsubscript{2}-i bi layer CdS/CdTe solar cell is the base line device to be used as a bench mark for this work.
5.4.2 Effect of CdS Thickness on SnO$_2$:F and ITO/SnO$_2$-i CdS/CdTe Solar Cells

To date CdS/CdTe solar cell photocurrents have reached 86% of their 30.6 mA/cm$^2$ theoretical maximum for the 100 mW/cm$^2$ terrestrial spectrum. A significant photocurrent loss about 5 mA/cm$^2$ is due to window layer CdS band gap absorption below 520 nm depending on the thickness of the CdS layer. The thickness of the CdS layer could be decreased to reduce the photocurrent loss considerably but there appears to be a process dependent “critical CdS thickness” between 400 to 1000 Å below which the junction parameters degrade significantly [25]. X-ray diffraction and opto-electronic measurements of the interfacial region in high efficiency cells show that the photovoltaic active layer consists of a nearly homojunction of n-CdS$_{1-y}$Te$_y$/p-CdTe$_{1-x}$S$_x$/p-CdTe. The CdS$_{1-y}$Te$_y$ and CdTe$_{1-x}$S$_x$ alloys form via diffusion across the interface during CdTe deposition and post-deposition treatments and affect the photocurrent and junction behavior. The interfacial values of $x$ and $y$ correspond to the solubility limits in the CdTe-CdS system at the device processing temperature. Formation of the CdS$_{1-y}$Te$_y$ alloy on the S-rich side of the junction reduces the band gap and increases absorption, reducing photocurrent below 520nm. Formation of the CdTe$_{1-x}$S$_x$ alloy on the Te-rich side of the junction reduces the absorber layer band gap, due to the optical bowing parameter of the CdTe-CdS alloy system. The increase in long wavelength spectral response increases the photocurrent by $\sim$ 0.5 mA/cm$^2$, which is nearly offset by small reduction in $V_{oc}$ $\sim$ 25 mV. On the other hand, non-uniform consumption of CdS leads to parallel junctions between CdTe$_{1-x}$S$_x$/CdS$_{1-y}$Te$_y$ and CdTe$_{1-x}$S$_x$/ITO (or SnO$_2$), resulting in a net increase in $J_o$, which reduces $V_{oc}$. Penetration of S-rich species into the CdTe grain boundaries can produce a three dimensional junction, which increases the actual junction area, also reducing $V_{oc}$[18].

The thickness of the CdS layer should be sufficient enough to facilitate the optimum formation of these alloys to maintain good junction properties. So, as the thickness of the CdS is varied, the short circuit current density $J_{sc}$ decreases from thin to thick and $V_{oc}$ and FF deteriorate from thick to thin.
The thickness of CdS was varied in these devices by reducing the time of deposition of the film. The factor [1- QE] of the device at 450 nm is taken as a relative measure for the final thickness of CdS. The factor [1-QE @ 450nm] varies from low to high, as CdS thickness increases.

**Table 10. Device Parameters of SnO2 and ITO Solar Cells with Different CdS Thickness [34].**

<table>
<thead>
<tr>
<th>1-QE@ 450nm</th>
<th>( J_{sc} ) under 510 nm [mA/cm²] (average)</th>
<th>( V_{oc} ) [V] (average)</th>
<th>FF[%] (average)</th>
<th>( J_{sc} ) [mA/cm²] (average)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>ITO</td>
<td>SnO₂</td>
<td>ITO</td>
<td>SnO₂</td>
</tr>
<tr>
<td>0.25</td>
<td>4.51</td>
<td>4.46</td>
<td>0.785</td>
<td>0.790</td>
</tr>
<tr>
<td>0.36</td>
<td>4.10</td>
<td>3.76</td>
<td>0.826</td>
<td>0.815</td>
</tr>
<tr>
<td>0.48</td>
<td>3.48</td>
<td>3.16</td>
<td>0.830</td>
<td>0.833</td>
</tr>
<tr>
<td>0.55</td>
<td>2.82</td>
<td>2.98</td>
<td>0.820</td>
<td>0.820</td>
</tr>
</tbody>
</table>

**Figure 50. J-V Characteristics (left) Spectral Response (right) of the Best SnO₂/SnO₂-i Devices with Different CdS Thickness [34].**

Table 10 summarizes the device parameters of SnO₂ and ITO solar cells with varying CdS thickness, to be discussed further in this section. Figure 50 shows the J-V and
spectral response data for SnO$_2$ devices with varying CdS thickness and figure 51 shows the J-V and spectral response data for ITO devices with different CdS thickness.

![Graph showing J-V Characteristics and Spectral Response](image)

**Figure 51. J-V Characteristics (left) Spectral Response (right) of the Best ITO/SnO$_2$-i Devices with Different CdS Thickness [34].**

As expected the $J_{sc}$ under 510 nm decreased as the thickness of the CdS increased. The SnO$_2$ and ITO devices showed similar trend, however the $J_{sc}$s in ITO were slightly lower than that of SnO$_2$. The $V_{oc}$s and FF improved with increasing CdS thickness, implying better junction quality (see figure 52). The $R_{series}$ decreased with increase in CdS thickness. $R_{shunt}$ increased with CdS thickness, since thin CdS films may contain pinholes leading to direct contact of CdTe and SnO$_2$. However, the range of $R_{shunt}$ cannot explain the increase in FF(60 to 71%) from thin to thick CdS, therefore it is suggested that collection is the main limiting factor.
5.5 Effect of Substrate Temperature during CdTe CSS Deposition

A series of devices were fabricated to study the effect of CdTe deposition temperature, the substrate (SnO$_2$/CdS) temperature was increased from 580°C to 620°C, while keeping the source temperature constant at 660°C. Table 11 shows solar cell parameters for these cells.
Table 11. Device Parameters of SnO\textsubscript{2}:F /SnO\textsubscript{2}-i CdS/CdTe Solar cells with Different Substrate Temperature during CdTe CSS Deposition [34].

<table>
<thead>
<tr>
<th>CdTe Temperature [°C]</th>
<th>V\textsubscript{oc} [mV]</th>
<th>FF [%]</th>
<th>J\textsubscript{sc} [mA/cm\textsuperscript{2}]</th>
<th>R\textsubscript{series} [Ω\textperiodcentered cm\textsuperscript{2}]</th>
<th>R\textsubscript{shunt} [Ω\textperiodcentered cm\textsuperscript{2}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>580/660</td>
<td>830</td>
<td>77</td>
<td>23.00</td>
<td>0.32</td>
<td>3300</td>
</tr>
<tr>
<td>600/660</td>
<td>830</td>
<td>69</td>
<td>23.29</td>
<td>0.88</td>
<td>2500</td>
</tr>
<tr>
<td>610/660</td>
<td>760</td>
<td>69</td>
<td>23.82</td>
<td>0.53</td>
<td>1000</td>
</tr>
<tr>
<td>620/660</td>
<td>740</td>
<td>63</td>
<td>23.25</td>
<td>0.65</td>
<td>400</td>
</tr>
</tbody>
</table>

Figure 54. J-V Characteristics (left) and Spectral Response (right) of SnO\textsubscript{2}:F /SnO\textsubscript{2}-i CdS/CdTe Solar Cells with Different Substrate Temperature during CdTe CSS Deposition [34].
Figure 55. Effect of Different Substrate Temperatures during CSS CdTe Deposition on Device Parameters [34].

As seen in the figures 54 & 55, increasing the substrate temperature from 580 to 620°C, degraded the device parameters. The $V_{oc}$, FF and $R_{shunt}$ of the devices decreased with increase in substrate temperature ($T_{sub}$). CSS employs high substrate temperatures during film growth, which can promote the formation of larger grains and higher $V_{oc}$s yielding better device performance. However, as $T_{sub}$ increases, the thickness of the CdS layer reduces as can be seen from the spectral response of these devices (see figure 54), due to increased consumption of CdS by CdTe. The devices fabricated at $T_{sub}$ of 580 and 600°C show the same effect on CdS thickness but in the devices with higher $T_{sub}$, due to the increased non uniform consumption of CdS, the CdTe may be penetrating further into CdS leading to direct contact of CdTe and SnO$_2$ (see figure 56), causing shunting, there by resulting in lower $V_{oc}$s. So it can be concluded that it is not advisable to attempt to reduce the final thickness of CdS by increasing the CdTe deposition temperature, as it results in poor junction parameters.
Jordan and Albright developed a method to avoid shorting of CdTe and the SnO₂ (as described in the previous section) due to flaws in the CdS layer, by providing a conductive layer which is formed by two SnO₂ layers each having substantially dissimilar electrical conductivity, such that an electrically-conductive SnO₂ layer, interconnects the plurality of photovoltaic cells (in the case of a panel), while the low conductivity layer prevents shorting of the cell. The electron density of the low conductivity SnO₂ layer may be adjusted to be within approximately three orders of magnitude of the presumed electron density of the p-type CdTe layer, such that a energy producing junction is formed in any area of flaws in the CdS layer by the CdTe and the SnO₂ layer. In their work Cadmium was used to dope the low conductivity SnO₂, but Zinc may also be used [33].

In this section, the effect of such a front contact comprising a bilayer of dissimilar resistivities is studied by depositing a layer of SnO₂ doped with Zinc on standard highly conducting SnO₂:F and the results are discussed. On the MOCVD deposited SnO₂:F, a high resistance layer of SnO₂ was reactivity sputtered from a Sn target, with 25% O₂ in pure Ar, the total pressure being 3.0 mT, at 300°C. The temperature of 300°C was determined to be the optimum temperature. Zinc was added, from a Zn target. The doping concentration of Zinc was controlled by the amount of RF power supplied to the Zn sputtering source.
The SnO$_2$ was sputtered for two thicknesses of 500 and 2000 Å at two different Zinc concentrations of 5% and 10%. The device structure of these cells are shown in figure 57.

![Device Structure Diagram](image)

**Figure 57. Device Structure of SnO$_2$:F CdS/CdTe Solar Cells with Sputtered SnO$_2$ Doped with Zinc (SnO$_2$:Zn) as Buffer Layer.**

**Table 12. Device Parameters of SnO$_2$:F /SnO$_2$:Zn CdS/CdTe Solar Cells for SnO$_2$:Zn Layer Thickness of 500 Å.**

<table>
<thead>
<tr>
<th>%Zn</th>
<th>$V_{oc}$ [mV]</th>
<th>FF [%]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [Ω-cm$^2$]</th>
<th>$R_{series}$ [Ω-cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>830.3</td>
<td>65</td>
<td>23.57</td>
<td>750</td>
<td>1.46</td>
<td>12.8</td>
</tr>
<tr>
<td>5</td>
<td>672.1</td>
<td>55</td>
<td>21.50</td>
<td>600</td>
<td>2.24</td>
<td>7.9</td>
</tr>
<tr>
<td>10</td>
<td>672.5</td>
<td>53</td>
<td>22.10</td>
<td>400</td>
<td>2.76</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Table 11 summarizes the performance of devices with 500 Å of SnO$_2$:Zn layer. The J-V and spectral response of the devices are shown in figure 58. As can be seen from figures 58 and 59, the device with no Zn had the highest $V_{oc}$ and $J_{sc}$. The FF and $R_{shunt}$ decreased with increase in Zn concentration. The $R_{series}$ increased with increase in Zn concentration. The $J_{sc}$ for the device with 10% zinc was slightly higher than that of the device with 5% Zinc.
Figure 58. J-V Characteristics (Left) and Spectral Response (Right) of SnO$_2$:F/SnO$_2$:Zn CdS/CdTe solar cells for SnO$_2$:Zn Layer Thickness of 500Å [34].

From the spectral response, it can be seen that QE @ 450 nm showed an increase (even though it is a small change) with increasing Zn concentration. This might be attributed to the interdiffusion of Zn into the CdS layer. The Zn in the CdS layer forms an alloy Zn$_x$Cd$_{(1-x)}$S, whose band gap almost varies linearly with the atomic fraction of Zn(x). The band gap of CdS is around 2.4 eV and the band gap of ZnS is 3.8 eV.
Consequently as Zn from the SnO$_2$:Zn layer diffuses into and alloys with the CdS film, the band gap increases. This shifts the short wave length cutoff to a smaller value, which leading to an increase in $J_{sc}$ [16]. Cd could also be diffusing into the SnO$_2$ layer, making it more resistive at the same time and formation of ZnS is also a possibility. It can also be seen from the QE plot that the devices with higher concentrations of Zn suffer from collection losses which may be due to lowering of electric field in the CdTe due to modification of interface properties. In the devices with higher concentration of Zn the $V_{oc}$ drop is consistent with the light J-V of devices without a buffer layer, one possible explanation may be that the Zn in the SnO$_2$ layer could be in the form ZnO, and as CdS reacts with ZnO, the buffer layer might get shorted but this possibility does not explain the increase in $R_{series}$ with increase in Zn concentration.

<table>
<thead>
<tr>
<th>%Zn</th>
<th>$V_{oc}$ [mV]</th>
<th>FF</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [Ω-cm$^2$]</th>
<th>$R_{series}$ [Ω-cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>780</td>
<td>55</td>
<td>23.10</td>
<td>600</td>
<td>3.25</td>
<td>9.8</td>
</tr>
<tr>
<td>5</td>
<td>823</td>
<td>67</td>
<td>22.95</td>
<td>900</td>
<td>1.15</td>
<td>12.6</td>
</tr>
<tr>
<td>10</td>
<td>668</td>
<td>47</td>
<td>22.36</td>
<td>300</td>
<td>5.24</td>
<td>6.9</td>
</tr>
</tbody>
</table>

Figure 60. J-V Characteristics (Left) and Spectral Response (Right) SnO$_2$:F/SnO$_2$:Zn CdS/CdTe Solar Cells for SnO$_2$:Zn layer Thickness of 2000 Å [34].
Figure 61. Change in Device parameters of SnO₂:F/SnO₂:Zn CdS/CdTe solar cells for Different Concentrations of Zinc (SnO₂:Zn layer thickness of 2000 Å) [34].

Table 12 summarizes the performance of devices with 2000 Å of SnO₂:Zn layer. Figure 59 shows the J-V and spectral response data for these devices. The device with no zinc exhibited low Voc and FF, though higher than the device with 10% Zn. This may be a bad device and the data pertaining to this device can be discarded as an anomaly because devices with 1000 Å of sputtered SnO₂ showed excellent device performance [27]. The device with 5% Zn displayed highest Voc and FF and did not suffer from collection losses in the red region. The device with 10% Zn showed a marked increase in the QE in the below 520 nm, due to the formation of the alloy ZnₓCd₁₋ₓS as described in the previous paragraphs. This device also suffered from pronounced collection loss in the red region. It can be seen that small amounts of Zn in thicker SnO₂ layer seemed to increase device performance. It should be remembered that the device with no zinc could also be as good as this device with 5% device, if not better.

5.7 CdS/CdTe Solar Cells with Indium Oxide as Buffer Layer

5.7.1 SnO₂:F/In₂O₃ CdS/CdTe Solar Cells

To study the effect of In₂O₃ as buffer layer, 2000 Å of reactively sputtered In₂O₃ at a temperature of 300°C was deposited on, MOCVD deposited SnO₂:F at 460°C (standard SnO₂:F) and the device was completed as given in the device structure in figure 62.
Figure 62. Device Structure of SnO$_2$:F/In$_2$O$_3$ CdS/CdTe Solar Cell.

To determine the influence of the surface properties of In$_2$O$_3$, a series of devices were fabricated (a) SnO$_2$:F/In$_2$O$_3$ (b) SnO$_2$:F/In$_2$O$_3$ annealed at 600°C (c) SnO$_2$:F/In$_2$O$_3$/SnO$_2$ annealed at 600°C, all these devices were completed with CBD grown CdS, standard CSS CdTe and contacted with doped graphite, conforming to the device structure given above. The performance of the devices are summarized in table 14.

Table 14. Device Parameters of SnO$_2$:F cells with In$_2$O$_3$ as Buffer Layer [34].

<table>
<thead>
<tr>
<th>Front contact</th>
<th>$V_{oc}$ [mV]</th>
<th>FF[%]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [Ω-cm$^2$]</th>
<th>$R_{series}$ [Ω-cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$:F+In$_2$O$_3$ Not annealed</td>
<td>827</td>
<td>67</td>
<td>22.75</td>
<td>1100</td>
<td>0.74</td>
<td>12.6</td>
</tr>
<tr>
<td>SnO$_2$:F+In$_2$O$_3$ Annealed at 600°C in He</td>
<td>825</td>
<td>53</td>
<td>21.46</td>
<td>800</td>
<td>1.56</td>
<td>9.4</td>
</tr>
<tr>
<td>SnO$_2$:F+In$_2$O$_3$ +SnO$_2$ Annealed at 600°C in He</td>
<td>841</td>
<td>63</td>
<td>22.1</td>
<td>1250</td>
<td>0.86</td>
<td>11.7</td>
</tr>
</tbody>
</table>
Figure 63. I-V Characteristics (Left) and Spectral Response (Right) of SnO$_2$:F Cells with In$_2$O$_3$ as Intrinsic Layer.

The device in which the SnO$_2$:F/In$_2$O$_3$ bi-layer was annealed at 600°C in He, showed evidence of a barrier formation, an effect similar to the ITO devices without the high resistance layer and when the In$_2$O$_3$ layer was “encapsulated” by a layer of CVD deposited intrinsic layer and the tri-layer was annealed at 600°C in He, the device did not show any barrier formation, although the device exhibited higher series resistance due to the addition of a 3000Å layer of SnO$_2$-i layer as expected, confirming that the barrier formation was due to the surface properties of In$_2$O$_3$ layer which appear to be sensitive to processing. The best device was the one with as deposited SnO$_2$/In$_2$O$_3$ bi-layer, suggests that In$_2$O$_3$ can be used as buffer layer in CdS/CdTe solar cells.

5.7.2. ITO/In$_2$O$_3$ CdS/CdTe Solar Cells

In this section, results for ITO/In$_2$O$_3$ based devices are discussed. CdS/CdTe solar cell was fabricated with 2000 Å of ITO sputtered at 200°C in Ar as front contact and 250 to 2000 Å of reactively sputtered In$_2$O$_3$ (at 300°C) in Ar/O$_2$ mixture (25% O$_2$) from Indium target was deposited on it as the buffer layer. The device was then completed conforming to the device structure given below.
Table 15. Device Parameters of ITO/In$_2$O$_3$ Cells with ~800 Å of CdS.

<table>
<thead>
<tr>
<th>Thickness of In$_2$O$_3$ [Å]</th>
<th>$V_{oc}$ [mV]</th>
<th>FF [%]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [Ω·cm$^2$]</th>
<th>$R_{series}$ [Ω·cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>830</td>
<td>0.66</td>
<td>24.14</td>
<td>2000</td>
<td>0.76</td>
<td>13.22%</td>
</tr>
<tr>
<td>500</td>
<td>840</td>
<td>0.64</td>
<td>23.49</td>
<td>1666</td>
<td>0.77</td>
<td>12.71%</td>
</tr>
<tr>
<td>1000</td>
<td>830</td>
<td>0.67</td>
<td>23.56</td>
<td>2000</td>
<td>0.53</td>
<td>13.17%</td>
</tr>
<tr>
<td>2000</td>
<td>830</td>
<td>0.62</td>
<td>23.00</td>
<td>2500</td>
<td>1.10</td>
<td>11.89%</td>
</tr>
</tbody>
</table>

The solar cell characteristics for devices different thickness of In$_2$O$_3$ are listed in table 15. Performance of the best devices is summarized in the following table. Figures 65 and 66 show the I-V and Spectral response characteristics of these devices respectively.

As the thickness of the In$_2$O$_3$ layer increases, the $V_{oc}$s remain fairly constant about 830 mV. The series resistance of the devices is expected to increase with the increase in the thickness of the high resistance In$_2$O$_3$ layer; in general, this is true but the device with 1000Å of In$_2$O$_3$ does not fit the trend. The 0 Å device shows the barrier formation as discussed earlier. The FFs also follow a similar trend, decreasing with the increase of thickness of the buffer layer with the exception of the 1000 Å device having the highest fill factor.
Figure 65. I-V Characteristics (Left) and Spectral Response (Right) ITO/In$_2$O$_3$ Cells with 800 Å of CdS.

Figure 66. Change in Device Parameters of ITO/In$_2$O$_3$ Cells with 800 Å of CdS with Change in Thickness of In$_2$O$_3$ [34].

The $R_{shunt}$ of the devices, initially decreased from 250Å device to 500Å device, but increased with increase in thickness then on. The highest value for shunt resistance was for the device with 2000 Å of In$_2$O$_3$. The $J_{sc}$s are fairly similar as seen from the spectral response characteristics.
5.8 Effect of the CdS Thickness on ITO/In$_2$O$_3$ Devices

In order to determine the effectiveness of In$_2$O$_3$ as a buffer layer, several CdTe cells were fabricated with CdS of varying thickness. Specifically, using the same range of In$_2$O$_3$ thickness, CdS was deposited for a thickness of approximately 700, 600, 500 Å.

**Table 16. Device Parameters of ITO/In$_2$O$_3$ Cells with ~700 Å of CdS.**

<table>
<thead>
<tr>
<th>Thickness of In$_2$O$_3$ [Å]</th>
<th>$V_{oc}$ [mV]</th>
<th>FF [%]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [Ω-cm$^2$]</th>
<th>$R_{series}$ [Ω-cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>830</td>
<td>67</td>
<td>23.64</td>
<td>2000</td>
<td>0.77</td>
<td>13.1</td>
</tr>
<tr>
<td>500</td>
<td>840</td>
<td>66.4</td>
<td>23.08</td>
<td>1666</td>
<td>0.78</td>
<td>12.8</td>
</tr>
<tr>
<td>1000</td>
<td>820</td>
<td>70.5</td>
<td>23.76</td>
<td>2500</td>
<td>0.55</td>
<td>13.6</td>
</tr>
<tr>
<td>2000</td>
<td>840</td>
<td>67</td>
<td>22.86</td>
<td>3500</td>
<td>1.14</td>
<td>12.9</td>
</tr>
</tbody>
</table>

**Table 17. Device Parameters of ITO/In$_2$O$_3$ Cells with ~600 Å of CdS.**

<table>
<thead>
<tr>
<th>Thickness of In$_2$O$_3$ [Å]</th>
<th>$V_{oc}$ [mV]</th>
<th>FF [%]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [Ω-cm$^2$]</th>
<th>$R_{series}$ [Ω-cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>820</td>
<td>71.9</td>
<td>24.04</td>
<td>2000</td>
<td>0.76</td>
<td>14.2</td>
</tr>
<tr>
<td>500</td>
<td>810</td>
<td>70.9</td>
<td>23.66</td>
<td>2000</td>
<td>0.90</td>
<td>13.6</td>
</tr>
<tr>
<td>1000</td>
<td>800</td>
<td>66.4</td>
<td>22.58</td>
<td>800</td>
<td>0.44</td>
<td>12.0</td>
</tr>
<tr>
<td>2000</td>
<td>810</td>
<td>70.5</td>
<td>23.98</td>
<td>2000</td>
<td>0.47</td>
<td>13.7</td>
</tr>
</tbody>
</table>

**Table 18. Device Parameters of ITO/In$_2$O$_3$ Cells with ~500 Å of CdS.**

<table>
<thead>
<tr>
<th>Thickness of In$_2$O$_3$ [Å]</th>
<th>$V_{oc}$ [mV]</th>
<th>FF [%]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [Ω-cm$^2$]</th>
<th>$R_{series}$ [Ω-cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>790</td>
<td>63.0</td>
<td>25.09</td>
<td>1600</td>
<td>0.89</td>
<td>12.4</td>
</tr>
<tr>
<td>500</td>
<td>820</td>
<td>64.0</td>
<td>24.81</td>
<td>1400</td>
<td>1.26</td>
<td>13.0</td>
</tr>
<tr>
<td>1000</td>
<td>810</td>
<td>60.0</td>
<td>24.31</td>
<td>1100</td>
<td>0.92</td>
<td>11.4</td>
</tr>
<tr>
<td>2000</td>
<td>710</td>
<td>62.8</td>
<td>23.92</td>
<td>1250</td>
<td>0.51</td>
<td>10.6</td>
</tr>
</tbody>
</table>
Figure 67. I-V Characteristics (Left) and Spectral Response (Right) ITO/In$_2$O$_3$ Cells with 700 Å of CdS.

Figure 68. I-V Characteristics (Left) and Spectral Response (Right) ITO/In$_2$O$_3$ Cells with 600 Å of CdS.
Figure 69. I-V Characteristics (Left) and Spectral Response (Right) ITO/In₂O₃ Cells with 500 Å of CdS.

Figure 70. Change in Device Parameters of ITO/In₂O₃ Cells with 700 Å of CdS with Change in Thickness of In₂O₃ [34].

Figures 67, 68, and 69 show the J-V characteristics and spectral response of the ITO/In₂O₃ devices with 700, 600 and 500 Å of CdS respectively. Tables 16, 17 and 18 and figures 70, 71, 72 summarize the device parameters of these devices.
As seen from all the figures given above, the following conclusions can be made. The parameters of the devices with 700 Å of CdS are very much similar to those of 800 Å. From the spectral response plots of all the devices, it can be seen that the blue region shows CdS thickness effect and the red region is essentially identical.
All the devices without the buffer layer, i.e., 0 Å of In$_2$O$_3$ show the barrier formation at the ITO/CdS interface (the 0 Å device of the 600 Å CdS set was a bad device and hence was excluded from the plots).

Considering all the data, there does not seem to be any trend for $R_{\text{series}}$, with In$_2$O$_3$ thickness or CdS thickness, even though it was suggested earlier that In$_2$O$_3$ thickness had an effect on $R_{\text{series}}$. $R_{\text{shunt}}$ is lower for thin CdS devices. The $V_{\text{oc}}$s start to decrease for CdS thickness of 600 Å and become considerably lower for devices with 500 Å of CdS. The $J_{\text{sc}}$s increase as CdS thickness decreases. This is typical as seen with baseline devices in previous sections of this chapter. However, the thin CdS set results suggest that increasing the In$_2$O$_3$ thickness degrades solar cell performance. Almost all the QE data for devices with thicker In$_2$O$_3$ (1000 Å and 2000 Å) display collection losses due to deeply penetrating photons. The highest efficiency of 14.2 % was achieved for the device with 250 Å of In$_2$O$_3$ and a CdS thickness of approximately 600Å. This suggests that In$_2$O$_3$ can be used as buffer layer in CdTe solar cells successfully.

5.9 Window less Junctions

In this section, the performance of different TCO-CdTe junctions have been explored. Devices were made with different TCOs as front contact without the window layer CdS. So a direct junction was formed between n-type TCO and CdTe. The device structure of these devices is as follows

![Figure 73. Device Structure of TCO/CdTe Solar Cell.](image)

Cd$_2$SnO$_4$ (CTO) thin films were sputtered from oxide targets at room temperature in Ar ambient. The as deposited films were amorphous but subsequent annealing in He at 600°C rendered the film poly crystalline in inverse spinel structure with preferred
orientation of <222>. The properties of the 2000 Å film after annealing, discussed in this section are listed in table 19.

Devices were made with three types of CTO: (1) as deposited CTO film, (2) annealed CTO film and (3) annealed CTO film with a buffer layer of CVD SnO₂ of about 3000Å in thickness, all the devices were then completed conforming to the device structure in figure 72. Since the CdS window layer is not present in these devices, the quality of junction formed between TCO and CdTe turned out very poor and devices were suffering from very high series resistance and extremely low shunt resistance. The performance of the CTO devices is listed in table 20.

**Table 19. Properties of Spinel TCOs.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Annealing at 600 C in He</th>
<th>Metallic ratio</th>
<th>Film crystallinity</th>
<th>Resistivity in Ω-cm</th>
<th>Average transmission in visible region</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZTO at 450°C</td>
<td>No</td>
<td>~2 Zn/Sn</td>
<td>Amorphous</td>
<td>4.3 X 10⁻³</td>
<td>90%</td>
</tr>
<tr>
<td>C*</td>
<td>Yes</td>
<td>~2 Zn/Sn</td>
<td>Polycrystalline in inverse spinel</td>
<td>6.6 X 10⁻²</td>
<td>92%</td>
</tr>
<tr>
<td>CTO at RT</td>
<td>yes</td>
<td>~2 Cd/Sn</td>
<td>Polycrystalline in inverse spinel</td>
<td>3.9 X 10⁻⁴</td>
<td>89%</td>
</tr>
<tr>
<td>CdInO₃ at 200°C</td>
<td>yes</td>
<td>~1 Cd/In</td>
<td>Polycrystalline</td>
<td>7.35 X 10⁻⁴</td>
<td>89%</td>
</tr>
<tr>
<td>CdIn₂O₄ at RT</td>
<td>yes</td>
<td>~0.5 Cd/In</td>
<td>Polycrystalline in normal spinel</td>
<td>4.6 X 10⁻⁴</td>
<td>90%</td>
</tr>
</tbody>
</table>

*taken from [27]

The device with the as deposited CTO was inferior to the devices with annealed CTO because the as deposited film was amorphous and highly resistive. When the film was annealed, the film became highly conductive leading to higher J_{sc}s and improved V_{oc}.
With the addition of a high resistivity buffer layer of CVD deposited SnO₂, the $V_{oc}$ improved further but the $J_{sc}$ decreased. All the films showed very high shunting (due to high leakage currents due to poor junction formation), and the shunt resistance improved with the incorporation of buffer layer.

**Table 20. Device Parameters of Spinel TCO/CdTe Devices.**

<table>
<thead>
<tr>
<th>Front Contact</th>
<th>Annealed in He at 600°C (spinel TCO)</th>
<th>Buffer layer</th>
<th>$V_{oc}$ [mV]</th>
<th>FF</th>
<th>$J_{sc}$ [mA/cm²]</th>
<th>Rsh [Ω-cm²]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CTO</td>
<td>No</td>
<td>No</td>
<td>174</td>
<td>0.320</td>
<td>13.69</td>
<td>47</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>yes</td>
<td>No</td>
<td>299</td>
<td>0.315</td>
<td>22.05</td>
<td>68</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>CVD SnO₂ 3000Å</td>
<td>454</td>
<td>0.300</td>
<td>17.33</td>
<td>101</td>
<td>2.33</td>
</tr>
<tr>
<td>SnO₂:F</td>
<td>No</td>
<td>ZTO</td>
<td>330</td>
<td>0.356</td>
<td>17.3</td>
<td>149</td>
<td>2.05</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>ZTO</td>
<td>463</td>
<td>0.353</td>
<td>22.06</td>
<td>140</td>
<td>3.61</td>
</tr>
<tr>
<td>CdInO₃</td>
<td>yes</td>
<td>-</td>
<td>240</td>
<td>0.200</td>
<td>12.94</td>
<td>44</td>
<td>0.64</td>
</tr>
<tr>
<td>CdIn₂O₄</td>
<td>yes</td>
<td>-</td>
<td>310</td>
<td>0.385</td>
<td>14.67</td>
<td>135</td>
<td>3.86</td>
</tr>
</tbody>
</table>

In order to study the junction between Zn$_2$SnO₄ (ZTO) and CdTe, devices were made with SnO₂: F as front contact with a thin layer of ZTO as buffer layer. The ZTO films were sputtered from oxide targets at 450°C in Ar. The as deposited film was amorphous and when subjected to annealing in He at 600°C it became polycrystalline in the inverse spinel structure. The films were not deposited at room temperature like CTO because, the as deposited films at room temperature did not become polycrystalline even after annealing at 600°C in He. The film seemed to require more energy to crystallize. So it was deposited at the highest temperature possible at the sputtering chamber. The films became more resistive after annealing, but the device with annealed ZTO layer was better than the device with the as deposited layer, in terms of $V_{oc}$ and $J_{sc}$. The device parameters
of these devices are listed in table 20. To study the junction between Cadmium Indium Oxide (CIO) and CdTe, CIO was deposited from Cadmium and Indium target in 25% O₂ with pure Ar. The properties of the film are listed in table 20. Though both the devices suffered from heavy shunting and series resistance effects the device with Cd to In ratio of 0.5 was more efficient than the device with Cd to In ratio of 1:1, with an efficiency of 3.8%, offering sufficient incentive to study and develop this TCO further, for use in CdTe solar cells. All the devices were extremely poor with low shunt and high series resistances. All QE plots showed consistent collection losses at higher wavelengths.

![Diagram](image1)

**Figure 74.** Spectral Response of CTO/CdTe Cells (left) and SnO₂/ZTO/CdTe Devices (right).

![Diagram](image2)

**Figure 75.** Spectral Response of CIO/ CdTe Devices.
CHAPTER 6
CONCLUSION

In the previous chapter, SnO$_2$:F and ITO- the two most popular choices as front contacts to CdTe solar cells were compared. It can be observed that the ITO film with only 2000 Å thickness (1/3 rd of the thickness of standard SnO$_2$) lead to excellent device performance on par with the standard SnO$_2$ devices. Devices made with both SnO$_2$ and ITO without a high resistance buffer layer had low device parameters but ITO showed a barrier formation at the CdS/ITO interface, leading to large series resistance. So within reasonable limits, it can be concluded that ITO by itself (without a buffer layer) is not an effective as front contacts for CdTe solar cells, but considering the facts that devices without buffer layers performed poorly in either case (SnO$_2$ and ITO), and barrier formation was not observed when a high resistivity buffer layer was included, this conclusion would not be a deterrent for the use of ITO as front contact in solar cell applications.


<table>
<thead>
<tr>
<th>TCO</th>
<th>Buffer layer(2000Å)</th>
<th>$V_{oc}$ [mV]</th>
<th>FF</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [$\Omega$-cm$^2$]</th>
<th>$R_{series}$ [$\Omega$-cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$:F CVD(3000 Å)</td>
<td>SnO$_2$-Sputtered</td>
<td>830</td>
<td>0.77</td>
<td>23.0</td>
<td>3300</td>
<td>0.32</td>
<td>14.7%</td>
</tr>
<tr>
<td>SnO$_2$:F MOCVD at 460°C</td>
<td>SnO$_2$:Zn (5%)-sputtered</td>
<td>780</td>
<td>0.55</td>
<td>23.1</td>
<td>600</td>
<td>3.25</td>
<td>9.84%</td>
</tr>
<tr>
<td></td>
<td>In$_2$O$_3$-sputtered</td>
<td>823</td>
<td>0.67</td>
<td>22.9</td>
<td>900</td>
<td>1.15</td>
<td>12.67%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>827</td>
<td>0.67</td>
<td>22.7</td>
<td>1100</td>
<td>0.74</td>
<td>12.60%</td>
</tr>
</tbody>
</table>
The performance of SnO$_2$: F/CdS/CdTe devices with different high resistance buffer layers were explored and the best devices are summarized in table 21. All the devices had standard 800 Å CBD CdS, 5 µm thick CSS CdTe and doped graphite back contact. As can be seen from table 21, the use of In$_2$O$_3$ as high resistivity layer resulted in decent device performance. Also it might seem from the table that the best performance was achieved for the device with MOCVD SnO$_2$ as intrinsic layer, but a similar performance was achieved for devices with thinner layer of sputtered SnO$_2$ (see table 22).

**Table 22. SnO$_2$: F/CdS/CdTe Devices with Thin Sputtered SnO$_2$ Buffer Layer.**

<table>
<thead>
<tr>
<th>TCO</th>
<th>Sputtered SnO$_2$-i</th>
<th>$V_{oc}$ [mV]</th>
<th>FF[%]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [Ω-cm$^2$]</th>
<th>$R_{series}$ [Ω-cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$:F</td>
<td>250 Å*</td>
<td>847.0</td>
<td>72.5</td>
<td>23.72</td>
<td>2200</td>
<td>0.63</td>
<td>14.60</td>
</tr>
<tr>
<td></td>
<td>500 Å</td>
<td>830.3</td>
<td>65.6</td>
<td>23.57</td>
<td>750</td>
<td>1.46</td>
<td>12.84</td>
</tr>
</tbody>
</table>

* Taken from reference 27.

The performance of the best ITO devices with MOCVD SnO$_2$ and sputtered In$_2$O$_3$ are summarized in the table below. Since ITO devices with sputtered SnO$_2$ were not studied, it can be expected within reasonable limits that ITO devices with thin sputtered SnO$_2$ as buffer layer would also lead to excellent device parameters comparable to the values listed in table 22.

**Table 23. ITO / CdS/CdTe Devices with Different Buffer Layers**

<table>
<thead>
<tr>
<th>TCO</th>
<th>Buffer layer</th>
<th>$V_{oc}$ [mV]</th>
<th>FF[%]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [Ω-cm$^2$]</th>
<th>$R_{series}$ [Ω-cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO sputtered</td>
<td>SnO$_2$</td>
<td>820</td>
<td>69</td>
<td>22.1</td>
<td>3300</td>
<td>0.53</td>
<td>12.53%</td>
</tr>
<tr>
<td></td>
<td>MOCVD(3000Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>In$_2$O$_3$</td>
<td>(2000 Å)</td>
<td>830</td>
<td>62</td>
<td>23.0</td>
<td>2500</td>
<td>1.10</td>
</tr>
</tbody>
</table>

ITO devices with, thin sputtered In$_2$O$_3$ layer as the buffer layer also had decent performance. Table 24 summarizes the best devices with thick CdS and table 25 summarizes the best devices with thin CdS. As seen from table 24, the devices with 250 Å and 1000 Å of In$_2$O$_3$ have almost similar good performance, for relatively thick CdS. But in the case of thinner CdS devices, devices with thicker In$_2$O$_3$ layer displayed lower device parameters. However, in either case (ITO/ In$_2$O$_3$ devices with thick or thin CdS),
the use of thin In$_2$O$_3$, resulted in good device parameters consistently. The best efficiency was achieved for the device with only 250 Å of In$_2$O$_3$ and 600 Å of CdS with an efficiency of 14.2 %, even when the thickness of CdS was further reduced, the device performance was appreciable with an efficiency of 13% for a In$_2$O$_3$ thickness of 500 Å (see table 25). However as often is the case $J_{sc}$ gains were offset by lower $V_{oc}$s and FFs.

**Table 24. Summary of Best ITO/In$_2$O$_3$ Devices with Thick CdS Layer.**

<table>
<thead>
<tr>
<th>TCO</th>
<th>In$_2$O$_3$ thickness[Å]</th>
<th>CdS thickness[Å]</th>
<th>$V_{oc}$ [mV]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [Ω·cm$^2$]</th>
<th>$R_{series}$ [Ω·cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO sputtered</td>
<td>250</td>
<td>800</td>
<td>830</td>
<td>66</td>
<td>24.14</td>
<td>2000</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td></td>
<td>830</td>
<td>67</td>
<td>23.56</td>
<td>2000</td>
<td>0.53</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>700</td>
<td>830</td>
<td>67</td>
<td>23.64</td>
<td>2000</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td></td>
<td>820</td>
<td>71</td>
<td>23.76</td>
<td>2500</td>
<td>0.55</td>
</tr>
</tbody>
</table>

**Table 25. Summary of Best ITO/In$_2$O$_3$ Devices with Thin CdS Layer.**

<table>
<thead>
<tr>
<th>TCO</th>
<th>In$_2$O$_3$ thickness[Å]</th>
<th>CdS thickness[Å]</th>
<th>$V_{oc}$ [mV]</th>
<th>$J_{sc}$ [mA/cm$^2$]</th>
<th>$R_{shunt}$ [Ω·cm$^2$]</th>
<th>$R_{series}$ [Ω·cm$^2$]</th>
<th>Eff [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO sputtered</td>
<td>250</td>
<td>600</td>
<td>820</td>
<td>72</td>
<td>24.04</td>
<td>2000</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>500</td>
<td>790</td>
<td>63</td>
<td>25.09</td>
<td>1600</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td></td>
<td>820</td>
<td>64</td>
<td>24.81</td>
<td>1400</td>
<td>1.26</td>
</tr>
</tbody>
</table>

Since the loss of $J_{sc}$ due to the absorption of CdS layer in the below 520 nm region of the visible spectrum is an important issue, when it comes to improving, the CdTe solar cell efficiency, this performance of ITO/In$_2$O$_3$ CdTe solar cells seems like a promising possibility.

Co sputtering offered an opportunity to deposit and study the effects of ternary spinel TCOs, which is dealt with in the windowless junctions section of the previous chapter, the junction between different ternary spinel oxides and CdTe layers was explored. The SnO$_2$:F/ZTO/CdTe device had an efficiency of 3.6% and so did the CdIn$_2$O$_4$/CdTe device. The Cd$_2$SnO$_4$/CdTe device had an efficiency of 2.1% and the device performance improved after the inclusion of MOCVD deposited SnO$_2$ as intrinsic layer with an efficiency of 2.4%. The Ternary TCOs have to be studied further, especially Cd$_2$SnO$_4$ and Zn$_2$SnO$_4$ TCOs to achieve the highest efficiency for CdTe solar cells.
REFERENCES


[27]. R. Mamazza, “Ternary Spinel Cd₂SnO₄, CdIn₂O₄, and Zn₂SnO₄ and Binary SnO₂ and In₂O₃ Transparent Conducting Oxides as Front Contact Materials for CdS/CdTe Photovoltaic Devices”, Electrical Engineering, University of South Florida, 2000


[34] The J_sc values from light J-V curves depend on the area measurements, which can vary ± 10 %, therefore wherever J_sc values are cited for comparison purposes, they are based on values obtained from the spectral response of the devices; SR measurements are based on NREL calibrated standards and J_sc values are accurate within a maximum error of ±3%