The preparation and properties of ITO/tin/silicon solar cells

This item was submitted to Loughborough University's Institutional Repository by the/an author.

Additional Information:

- A Doctoral Thesis. Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of Loughborough University.

Metadata Record: https://dspace.lboro.ac.uk/2134/10839

Publisher: © Rachmat Mulyadi

Please cite the published version.
This item was submitted to Loughborough University as a PhD thesis by the author and is made available in the Institutional Repository (https://dspace.lboro.ac.uk/) under the following Creative Commons Licence conditions.

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/
THE PREPARATION AND PROPERTIES OF
ITO/TIN/SILICON SOLAR CELLS

by

Rachmat Mulyadi, drs

A Doctoral Thesis
Submitted in partial fulfilment of the
requirements for the award of Doctor of Philosophy
of the Loughborough University of Technology

July 1989.

Supervisor: R.D. Seager, MIEEE, AMIEEE

PREPARATION AND PROPERTIES OF ITO/TIN/SILICON SOLAR CELLS

by

Rachmat Mulyadi, drs

A Doctoral Thesis
Submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy of the Loughborough University of Technology

July 1989.

Supervisor: R.D. Seager, MIEEE, AMIEEE

To

My wife ERWINA
For her continuing support along the way
My son Andre for making the journey so enjoyable
ABSTRACT.

Transparent semiconducting oxide films of ITO have been deposited using screen printing techniques for fabricating heterostructure solar cells. The ITO material used is a ready-made combination of organometallic compounds of indium and tin, dissolved in a suitable organic vehicle to make a screen-printable ink or paste. The paste is then printed onto substrates in the desired configurations.

The effect of various firing temperatures, from 450 °C to 650 °C, on the film properties were observed. The sheet resistances, $R_s$, changed as the firing temperature varied. $R_s$ values could be decreased by annealing the films in an inert gas or in vacuum conditions. An annealing temperature of 300 °C seemed to be optimum for annealing the ITO films. This decreased the sheet resistance by a factor of more than ten. The lowest sheet resistance of the ITO films was about 290 Ω/sq, measured during annealing under vacuum conditions at a temperature of 300 °C. This gradually increased up to about 1 KΩ/sq after the film was aged for a few days in a laboratory atmosphere.

The solar cell structures of ITO/p-Si and ITO/Sn/p-Si were made in this research. The first structure suffered from an excessive oxide interfacial layer thickness and it was abandoned. The second structure was then made to overcome the problems resulting from the interfacial oxide. The Sn layer was produced by using evaporation prior to the screen printing of ITO. The thickness of the Sn layer was about 100 nm. After evaporation, screen printing methods were used to complete the heterostructure solar cell. The best typical values of these cells are, open circuit voltage, $V_{oc} = 0.360$ Volt, short circuit current density, $J_{sc} = 16.4$ mA/cm² with fill factor, $FF = 0.34$ and efficiency, $\eta = 2.5\%$ under 80 mW/cm² simulated illumination, where this illumination is equivalent to air mass 2, (AM2).
ii

CONTENTS

ABSTRACT

INDEX

ACKNOWLEDGMENTS

CHAPTER I : GENERAL INTRODUCTION

1.1 : Background

1.2 : Aim Of The Work

1.3 : Method Of Research

1.4 : Structure Of The Thesis

References

CHAPTER II : PHYSICS AND PROPERTIES OF SEMICONDUCTING OXIDE FILMS

2.1 : General View Of Transparent Conducting Oxides

2.2 : Possible Conduction Mechanism in Semiconducting Oxides

II.2.1 : Oxygen Deficient

II.2.2 : Doping Effect

2.3 : Electrical Properties

2.4 : Optical Properties

2.4.1 : Absorption

2.4.2 : Transmission

2.5 : Structure And Properties Some Semiconducting Oxide Films
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5.1</td>
<td>Tin Oxide (SnO₂)</td>
<td>43</td>
</tr>
<tr>
<td>2.5.2</td>
<td>Indium Oxide (In₂O₃)</td>
<td>47</td>
</tr>
<tr>
<td>2.5.3</td>
<td>Indium Tin Oxide (ITO)</td>
<td>51</td>
</tr>
<tr>
<td>2.6</td>
<td>Summary References</td>
<td>53</td>
</tr>
</tbody>
</table>

CHAPTER III: CONSTRUCTION AND PROPERTIES OF SOLAR CELLS 58

3.1 : Technical Review 58

3.1.1 : Band Model Of A Solar Cell 61

3.1.2 : The I/V Characteristics and Fill Factor 70

3.2 : Other Structure for Solar Cells 73

3.2.1 : Heterojunction 73

3.2.2 : Schottky Barrier 78

3.2.3 : MIS/SIS Heterostructure 81

(a) MIS Devices 82

(b) SIS Devices 85

3.3 : Some Reported Performances Of Semiconductor-Based Solar Cell Using Conductive Metal-Oxide window Layers 91

3.4 : The Role Of Thin Film in Solar Cell 94

3.5 : Summary References 98

CHAPTER IV: THICK FILM TECHNOLOGY 103

4.1 : The Development Of Thick Film Technology 103
CHAPTER V

4.2: The Deposition Process and Materials
4.3: The Printing Machine
  4.3.1: The Screen
  4.3.2: The Screen Mounting
  4.3.3: Substrate Holder
  4.3.4: Squeegee and Its Mechanism
4.4: Drying and Firing
4.5: Summary
  References

CHAPTER V: EXPERIMENTAL

5.1: Preparation Of ITO Films Using Screen
  Printing
  5.1.1. Screen Making
  5.1.2. Printing The Film
  5.1.3. Firing The Film
  5.1.4. Annealing
5.2: Electrical Characterization
  5.2.1. Sheet Resistance Measurement
  5.2.2. Hall Effect Measurement
5.3: Optical Characterization
5.4: Interfacial Layer Observation
5.5: Device Preparation
5.6: Summary
  References
CHAPTER VI: RESULTS AND DISCUSSION

6.1: Electrical Properties Of The ITO Film
   6.1.1. The Influence Of The Annealing
   6.1.2. Ageing
   6.1.3. Hall Effect Measurement
   6.1.4. Thickness Measurement

6.2: Discussions On The Electrical Properties Of The ITO FILM

6.3: Optical Properties

6.4: Structural Studies

6.5: Summary For ITO Films: Materials

6.6: Solar Cell Device Preparation
   6.6.1. Interfacial Layer Measurement
   6.6.2. Construction Of The ITO/p-Si Solar Cell
   6.6.3. Construction Of The ITO/Sn/p-Si Solar Cell
   6.6.4. Results Of The ITO/Sn/p-Si Solar Cell

6.7: Summary Of The Solar Cell Fabrication

REFERENCES

CHAPTER VII: CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

7.1: Introduction

7.2: Conclusions On The Material Studies
7.3 : Conclusions On The Solar Cell Fabrication

7.4 : Suggestions For Future Work

References

APPENDIX : Reprint Of The Article Entitled "Combinations Of Evaporation And Screen Printing Techniques For Fabricating ITO-Tin (Sn)-p Type Silicon Solar Cells. (To be published in Journal Of Solar Energy Materials)
ACKNOWLEDGMENTS

I would like to offer my sincere appreciation to all of my friends in the Electronic Component Group who made contribution in one way or another and it is not possible to mention by name all those who helped me.

I would like also to thank my supervisor Mr Rob. D. Seager for his advice and assistance and also to the Director of Research, Professor David. S. Campbell, during my research work.

Special thanks and grateful are also extended to The British Council for granting me the study leave and financial support for this research.

Without the technical support of the members of the Thin Film Physics, Surface Analysis Group and Material Engineering, my ideas would have remained ideas, and I am grateful to all of them. These thanks are also extended to The B.P. Solar International for their supporting facility.

Last but not least, I wish to offer my thanks and appreciation to Janet Stevenson for her continuing English support during making of this Thesis.
1
CHAPTER I.

GENERAL INTRODUCTION.

1.1. BACKGROUND.

Thin solid films, which are semitransparent to visible light and electrically conducting, have been observed for years. The need to develop these films was highlighted in the 1940's since the aircraft industries required transparent electrical heaters for windshield deicing. Since then, there has been a great interest in studying the materials and techniques used for producing semitransparent, electrically conducting films since the interest in interactions of light with electricity and electronically active materials has increased. The high transparency in the visible band region and high reflectivity in the near infrared region makes these films much more attractive for the basic development of a host of active and passive thin film applications such as coating on glasses, electrical contacts for liquid crystal displays or antistatic coatings on instrument panels. The films are also applicable in the field of solar energy.

Numerous significant new works then appeared, and various materials were used for different purposes. Many techniques such as evaporation, spraying, sputtering, chemical vapour deposition (CVD) and screen printing were investigated in
order to obtain the optimum properties of the films. The properties and characteristics of the thin films have been found to be different depending on how the atoms/molecules/ions/clusters of species are created for condensation or deposition\textsuperscript{[1,12,13]}\textsuperscript{1}. The same material deposited by two different techniques ordinarily yields widely differing sets of physical properties. This is due to the complex physics and chemistry of the materials used. Thin film materials may also be formed from a liquid or a paste, in which case it is called "thick film". It is not the thickness that is important in defining a film, but rather the way it is created with the consequential effects on its microstructure and properties.

Some of the film characteristics that are considered to be important for sophisticated applications are adhesion to the substrates, electrical resistivity, optical transmission versus wave-length, environmental stability, structure and morphology of the film surface, and chemical resistance or etchability of the films. It is known that these characteristics are useful in the application of these films to the production of solar energy.

1.2. AIM OF THE WORK.

The aim of this work is to study the possibility of fabricating solar cells by using thin metal films of Sn (tin), covered by semiconducting oxide films of indium tin oxide (ITO), deposited onto silicon substrates. Screen printing methods have been used by previous worker\textsuperscript{[8-10]} for depositing organometallic ITO pastes onto
silicon substrate for fabricating solar cells. Their work proved that there was photovoltaic effect in the devices producing electricity. Other work has been done on producing a similar device by evaporation\[^2\]. The work in this thesis investigates the possibility of combining these methods to produce higher efficiency in the solar cell. The methods which have been used here for depositing these two materials (i.e. Sn and ITO) are evaporation and screen printing thick-film techniques.

The use of screen printing techniques is accepted as the most cost effective method for cell metallisations in a production environment. Quite recently, this technique has been used for depositing a dopant for producing conventional p/n junction solar cells\[^{13-15}\] and depositing antireflection coatings to enhance the efficiency of the cells. Deposition of an organometallic material, ITO, onto silicon substrates for fabricating heterostructure solar cells has been undertaken by earlier researchers\[^{8-10}\]. The results found have been encouraging. It has been proved that photovoltaic effect in the device existed. It has also been discovered that firing conditions are the most critical parameters as they affect the development of electrical conduction of the films and also the growth of silicon dioxide between ITO and silicon substrates in the structure.

A survey into the properties of indium tin oxide films deposited from organometallic combination of indium and tin manufactured by Electro Science Laboratory (ESL) will be presented.
1.3. METHOD OF RESEARCH.

A review was made of the subject literature. It was found that compositions of indium and tin in the mixture of ITO materials play a major role in the electrical conduction of the films. A number of studies have been carried out in order to get the optimum compositions of ITO for a specific method of deposition. The composition range of 10% - 50% mole of SnO$_2$ in In$_2$O$_3$ has been investigated by Vossen$^{[5]}$, and it was reported that the lowest sheet resistance was found at the composition of 20% mole of SnO$_2$ in 80% mole In$_2$O$_3$ deposited using RF sputtering. The same compositions of 20% Sn in 80% In in the mixture of ITO films have also been reported by Mizuhashi$^{[16]}$ giving an optimum electrical conduction on which the films were deposited using reactive evaporation. The composition reported by Kane et.al$^{[7]}$ was 8% of Sn in 82% of In$_2$O$_3$, deposited using chemical vapour deposition (CVD). A spray deposition method for depositing ITO films was reported by Manifacier et.al$^{[17]}$ to have an atomic ratio Sn/In of 2-3% in the mixture. Compositional studies of the ITO films deposited from organometallic paste have been done by previous researchers using thick film screen-printing techniques$^{[9,18]}$. The studies were carried out using Auger electron spectroscopy. Elements detected at a depth of 120 nm were In = 35.7%, Sn = 5.0% and O = 55.1% for unannealed ITO films, and In = 20.5%, Sn = 3.8%, O = 52.2% for annealed films. Other components were not discussed.

Research into the fabrication of solar cells using semiconducting oxides has been intensified in the past few years.
The reason was to find alternatives to the conventional p/n junction solar cells which are already established. Tin oxide (SnO₂), indium oxide (In₂O₃), indium tin oxide (InₓSnₓO₃₋₉ /ITO) and cadmium orthostannate (Cd₂SnO₄) are examples of the common semiconducting oxides that are being extensively investigated for the fabrication of solar cells. Common models for fabricating solar cell devices using such materials are heterojunctions and MIS/SIS heterostructures. Various techniques for depositing such films have been established and yielded the range of solar cell efficiencies, η, from 0.3 to 12%²⁻⁴,¹⁹⁻²¹. Reports on ITO heterostructure solar cells prepared by screen printing are very limited, but the results have been encouraging⁸,⁹,¹⁰,¹⁸.

A combination of organometallic compounds, indium and tin, were dissolved in a suitable organometallic vehicle to make a screen printable ink or paste. The paste was then printed onto the substrates in the desired configuration. After heating in the moving-belt furnace the organic films decomposed producing a thin film of mixed semiconducting-oxide of In₂O₃/SnO₂ (commonly termed ITO) firmly bonded to the substrate. Firing temperatures were adjusted from 450 °C to 650 °C to meet the properties required for fabricating the solar cells. Optimum firing temperatures quoted by the manufacturer were 500 - 550 °C¹⁶,¹⁷ however, at a firing temperature as low as 450 °C electrical conduction was found to have developed.
1.4. STRUCTURE OF THE THESIS.

This thesis consisting of 7 chapters, begins with a short review of the materials and methods involved in the research as it is reviewed in this general introduction. The description of the semiconducting oxides including conduction mechanism is presented in chapter 2. This consists of studies which are directed into the main material of indium tin oxide and related materials. An attempt to explain the role of semiconducting oxides in conjunction with solar cell application is also presented in this chapter. This is associated with the approach of using screen printed thick-film for depositing ITO films from organometallic solution manufactured by ESL in fabricating solar cells.

The general physics of solar cells is presented in chapter 3. This is concerned with the physical principles and the operating characteristics of solar cell devices. Insight studies are stressed so that they may be used to understand the operation on specific devices which are used in thin film solar cells such as MIS/SIS heterostructures. Electronic junction, current transport and defining the efficiency are covered in this chapter.

Chapter 4, discusses a brief information of an introduction to the application of thick-film technology. Aparatus necessary for this technology are described. Details of the screen printing techniques and equipment are explained, and also the sequence of developing the properties of the films are discussed in this chapter.
Chapter 5, discusses the experimental procedures carried out in this work. It begins with the necessity for preparing the ITO films to be deposited from the organometallic paste onto the substrates. Artwork layout and patterning masks, which are required for producing the desired configuration of the films, are discussed. Electrical and optical characterization of the films are described. This chapter closes with studies of method of improving the film properties by annealing, and preparation to the fabrication of solar cell devices including interfacial layer observations between ITO films and silicon substrates.

Results are broadly discussed in chapter 6. This covers the effects of firing conditions and annealing of the films deposited onto several kinds of substrates such as glass, alumina and silicon. These processes are important for developing the properties of the films. Observations on ageing behaviour on the electrical property are noted. Physical and optical measurements are presented. The detailed construction of the ITO-Sn-p-silicon solar cells is analyzed followed by a qualitative discussion on the specific problems which have occurred in the experiments.

The conclusions of the work done in these experiments and the suggested work for further study are summarised in Chapter 7. It is believed that through optimisation and improved understanding of the properties of ITO materials and the structure it may be possible to obtain even better results.
REFERENCES.


CHAPTER II.

PHYSICS AND PROPERTIES OF SEMICONDUCTING OXIDE FILMS.

2.1. GENERAL VIEW OF TRANSPARENT CONDUCTING OXIDES.

The first industrial use for transparent and conductive films was 50 years ago when a transparent heating system was needed for deicing aircraft windscreens. Because of their large band-gap, these films are mainly used for optical windows as well as for transparent conductors. Some specific applications include antistatic coatings, high stability resistors, touch-sensitive switches, microwave shields and semitransparent mirrors. These films are also used in a great variety of digital displays and light emitting diode devices. For these applications, a low resistivity is more important than a high transparency. Indium tin oxide (ITO) is usually used, as it gives a higher conductivity[1].

Prospects in heat mirror systems need a structure having a high transparency in the visible band spectrum and high reflectivity in the infrared (IR) which overlay a substrate with high absorbance in the visible region. This is suitable for solar heating system applications. In the application of solar cell technology, these films are used as a transparent and conductive layer forming a space charge region in the underlying base semiconductor. In these devices, the thickness of the film can be
adapted to play the role of a very efficient antireflection coating (ARC).

There are two classes of materials that can form the thin film. These are semiconducting oxides and very thin films. The properties of the film from semiconducting oxides depend critically upon their oxidation state (stoichiometry) and the nature and quantity of impurities trapped in the film. However, the properties of thin film made of a very thin metal (≤ 50 Å) depend on film nucleation and initial coalescence phenomena.

The semiconducting oxides that have been used as transparent conductors include SnO₂, Sn₂O₃, CdO, Cd₂SnO₄, and these same materials doped at cation sites with Sb, In, Sn, Cd, Ti, Te, P or W and/or at anion sites with F or Cl. Not all of these materials are in general use, having proved to be undesirable in one way or another.

The conduction mechanisms in semiconducting oxides have not been explained satisfactorily up to the present time. They depend strongly on the manner of preparations and subsequent heat treatments in various ambients. Most attention has been focused on stoichiometric relationships, incorporation impurities and the presence of structure defects. All of the oxide materials that have been used for transparent conductors are known as n-type materials. Therefore, the following survey will be limited to n-type materials, and an approach will be made to some common oxides such as SnO₂ and In₂O₃ which is the nearest material to the
material used in the experiment ie. ITO.

2.2. POSSIBLE CONDUCTION MECHANISMS IN SEMICONDUCTING OXIDES.

2.2.1. Oxygen Deficient.

If a binary oxide is completely stochiometric, it is capable only of ionic conduction. Such materials are obviously of no interest as transparent conductors because of the high activation energy required for ionic conductivity. However, real oxides are rarely completely stochiometric. Many oxides because of an oxygen deficiency have an excess of electrons and thus exhibit some electronic conduction.

When a nonstochiometric oxide is oxygen deficient, the predominate defects may be either oxygen vacancies (oxygen deficit) or interstitial metal ions (excess metal), or both types of defects. Formation of these nonstochiometric defects usually only takes place at surfaces exposed to the ambient gas atmosphere[10]. This oxygen deficiency can be explained by the formation of oxygen vacancies in a stoichiometric material. In the process of removing an oxygen atom in such material, two electrons of the oxygen ion are left in the structure. If both of these electron are localized at the oxygen vacancy, such vacancies are neutral. If one or both of the localized electrons are excited and transferred away from the vacancy, the vacancy is left with an active positive charge with respect to the perfect crystal. The charged vacancy becomes an electron trapping site,
but in the process, one or more electrons are made available for conduction.

If oxygen vacancies predominate interstitial cations may be neglected, and thus the formula of an oxide, say \( \text{MO}_2 \), may be written \( \text{MO}_{2-y} \). If interstitial cations predominate, the composition of the oxide may be written \( \text{M}_{1+x}\text{O}_2 \), to emphasize that the defects represent an excess of metal rather than oxygen deficit to the stochiometric composition. If both types of defects are present in an oxygen deficient oxide, the formula may be written \( \text{M}_{1+x}\text{O}_{2-y} \). It may be noted that the formation of both oxygen vacancies and interstitial cations leads to the formation of complimentary quasi-free electrons. In oxygen deficient oxides the electronic conductivity is due to a transport of electrons. Therefore such electronic conductors can be termed n-type conductors.

For every electron released for conduction, somewhere there is a trap if the cation retains its original valence. Usually, the creation of anion vacancy results in a cationic valance charge. The conduction is considered to be efficient if the volume fraction of traps are small\(^{[2,8,10]}\), since these traps represent electrons available for conduction.

Typical free electron concentrations have been observed ranging from \(10^{17} - 10^{21} \text{ cm}^{-3}\). As has been mentioned, the volume of traps for electron conduction should be kept small even for at free electron concentrations of \(10^{21} \text{ cm}^{-3}\). Therefore, it is somewhat difficult to control the conductivity of the oxide.
materials by controlling the number of oxygen vacancies, since they are relatively easy to oxidise and reduce.

2.2.2. Doping Effects.

Electrical effects have been observed by various authors\cite{2,15,24} in a given host material with widely varying doping levels. It was found out that, in general, deposition processes that involve high substrate temperatures usually have an optimum doping level very much lower than processes that use low substrate temperatures. Other deposition process variables also have an effect on the optimum doping level. This in fact, is a result of the deposition process kinetics, rather than the actual quantity of dopant, determining the ratio of active to inactive dopant site, and of the number of oxygen vacancies created.

\( \text{In}_2\text{O}_3 \) is one of the many semiconducting oxides in which the electronic conduction can be increased by generating a non-stochiometric (oxygen deficient) structure or by doping the material with an impurity element so as to create an excess of electrons. This may be accomplished by substituting a higher valency cation (e.g. \( \text{Sn}^{+4} \) for \( \text{In}^{+3} \)) or by substituting a lower valency anion (e.g. \( \text{F}^{-1} \) for \( \text{O}^{2-} \)) in the lattice.

Since overall charge neutrality must be preserved, substitution of a higher valent cation requires the addition of an electron. Conversely, incorporation of a lower valent cation produces a hole. For example, if one incorporates \( \text{Sn}^{+4} \)
substitutionally in In₂O₃, an additional electron is added to the lattice. If, instead, Cd²⁺ is substitutionally added, a hole is produced, which in an n-type semiconductor becomes a trap.

Like oxygen vacancies, not all higher valent dopants incorporated into the lattice produce charge carriers. Some simply remain as neutral point defects. Electrically, equivalent effects can occur if anion sites are developed with atoms on which valence is lower than that of oxygen. The anion dopants of F⁻ and Cl⁻ are often employed.

Central to increasing conductivity by doping is the requirement that the dopant ion replace the appropriate host ion substitutionally in the host lattice. This implies that the ionic radius of the dopant must be the same size as or smaller than the ion it replaces, and that no compounds or solid solutions of dopant oxide with host oxide are formed. As an example, Ti⁴⁺ should have no effect on the conductivity of SnO₂, based on valence considerations alone, but TiO₂ forms a solid solution with SnO₂, resulting in a two-phase material with insulating occlusions.

In the absence of solid solution or compound formation, a dopant might still not be usable according to its ionic radius\(^8\). If the dopant ion is too large, an interstitial (rather than a substitutional) site is favoured, and the dopant will act as a scattering site rather than a source of charge carriers.
In the case of ITO, tin (Sn) has favourable size factor and will substitute readily for indium in the $\text{In}_2\text{O}_3$ lattice. The tin (Sn), therefore, will act as a donor, contributing electrons to a conduction band at room temperature$^{[12]}$.

2.3. ELECTRICAL PROPERTIES.

In general, the properties of semiconducting oxide films are dependent on composition, thickness and temperature ambient during deposition or post deposition. Film composition is determined by concentration of impurity additions in the compounds. It was noted by Aitchison$^{[6]}$ that impurity additions change the resistivity of the tin oxide films. The additions of indium oxide to the tin oxide increase the resistance and the additions of antimony oxide reduce the resistance of the films. Similar results were also noted by others including Vossen$^{[13]}$.

Substrate temperatures during deposition of Sn doped $\text{In}_2\text{O}_3$ films are characterised by Fan et.al$^{[14]}$ showing that the resistivity decreased for high temperatures. The resistivity decreases from $8 \times 10^{-4}$ ohm cm for a substrate temperature of 300 °C to about $2 \times 10^{-4}$ ohm cm for 600 °C. Also the carrier concentrations and Hall mobility are increase with increasing temperatures.

Work done by Mizuhashi$^{[15]}$ involves a high substrate temperature during deposition. He deposited ITO films onto soda lime glass using reactive evaporation (RE). The lowest resistivity found for
ITO films was $2 \times 10^{-4}$ ohm cm with carrier density $N_e$ of $1 \times 10^{21}$ cm$^{-3}$ and mobility, $\mu_H$, of 39 cm$^2$ V$^{-1}$ s$^{-1}$ at the optimized doping level 5 wt % of Sn into the indium oxide and the substrate temperature used was 400 °C. He also quoted that for pure indium oxide films, the values he found were, $\rho = 4 \times 10^{-4}$ Ω cm, carrier density $n_e = 4 \times 10^{20}$ cm$^{-3}$ and $\mu_H = 72$ cm$^2$ V$^{-1}$ s$^{-1}$. Compared to these values, characteristic features of ITO are higher in term of their carrier densities but low in mobility.

Experimenting done by the same author$^{[16]}$ used non-reactive evaporation for depositing the ITO films, with the substrate temperatures set at values from room temperature to 200 °C. Doping levels of SnO$_2$ in the ITO mixture ranged from 10 to 30 wt %. The electrical conduction properties, $N_e$ and mobility, showed a slight decrease compared to the previous experiment$^{[15]}$. The specific resistivity of the ITO films quoted was about $2 \times 10^{-3}$ Ω cm and the mobility had decreased to 10 cm$^2$ V$^{-1}$ s$^{-1}$. Also the carrier density became $N_e = 2 \times 10^{20}$ cm$^{-3}$.

The annealing temperature of post deposition of ITO deposited by dc-sputtering, according to Steckl et al.$^{[17]}$, can be divided into three regions. Increasing temperature in the first region (50 - 200 °C) results in a sharp drop in sheet resistance, and simultaneously, evidence of observable grain size is detected after a 200 °C anneal. Thus the effects observed in region I are that of a rapid increase in mobility associated with the process of crystallization. The temperature of 200 °C seems to be the transition point between the amorphous and polycrystalline
region. The range of temperature in the second region covers 200-500 °C. The change in the sheet resistance is roughly reversible, increasing during the heating cycle and decreasing during subsequent cooling (500 to 200 °C). The behaviour of sheet resistance in this region can be generalized on the basis of electron trapping by excess oxygen\textsuperscript{[18]}. In the final part, region three, where the annealing temperature is reducing 200 - 50 °C, the sheet resistance is constant with the annealing temperature. This possibly is because the temperature is too low to cause further diffusion and also lower the activation\textsuperscript{[19]}. This observation is drawn in Fig (2-1) in order to clarify the idea.

In view of the above analysis, the electrical properties are significantly affected by temperature either during deposition or post deposition. The effects of various annealing ambients such as air, oxygen, hydrogen, nitrogen and argon were extensively studied by Shanthi et al\textsuperscript{[21,27]} on undoped and antimony doped SnO\textsubscript{2} films, which had been prepared by spraying. They discovered a similar behaviour between the two films. The changes in resistivity due to annealing in various environments were, generally, caused by changes in mobility. The influence of temperature has also been observed by other researchers who noted similar occurrences\textsuperscript{[11,12,20]}.

The degradation to the electrical properties at higher tin (Sn) doping in In\textsubscript{2}O\textsubscript{3} have been stated by Agnihotri et al\textsuperscript{[24]} to be due to poor crystallinity. Small additions of Sn (up to 10 mole %) cause the resistivity to drop by providing more donors, but
Figure 2.1

The behaviour of sheet resistance under annealing temperature for post deposition ITO (Ref 17).
for additions greater than 10% the resistivity start to increase. The decrease in resistivity, when a small amount of Sn was added, is because every Sn atom is substitutionally incorporated in an In site releases one free electron to the matrix. This decrease ensues from the exchange of trivalent indium by quadrivalent tin within these substances. A lattice contraction is observed due to the incorporation of Sn. This suggests that the n-type conductivity is due to the replacement of In$^{3+}$ ions by Sn$^{4+}$ ions, which are smaller and are thus expected to cause contraction. Fan et al.\cite{14}, who worked on Sn-doped In$_2$O$_3$ films prepared by sputtering did, however, observe an expansion of the lattice. They stated that the n-type conductivity is not due to contraction which comes from the replacement of In$^{3+}$ ions by smaller Sn$^{4+}$ ions, but the expansion is observed consistently with the replacement of In$^{3+}$ by larger Sn$^{2+}$ ions and also with the incorporation of Sn ions in interstitial positions. In this case, the observed n-type conductivity could result from the excess electrons supplied by the interstitial Sn without a change in the Oxygen/In ratio. Substitution of Sn$^{2+}$ for In$^{3+}$ ions would decrease the electron concentration so that a stochiometric deficiency of oxygen would be necessary to explain the n-type conductivity. Therefore, the film composition would have to be represented by the formula $(\text{In}_1-x\text{Sn}_x)_2\text{O}_{3-y}$, and the carrier concentration would be proportional to $(y-x)$ since oxygen vacancies would act as donor centres.

An analysis made by Mizuhashi\cite{16} on putting the right doping concentration of Sn in In$_2$O$_3$ has shown a sharp decrease in the number of free carriers when a dopant concentration of more than
5 wt% is used. Lower concentrations of tin (4 - 6 wt%) liberate a great many carriers. Further addition, however, causes disorders in the In₂O₃ lattice. These disorders enhance the scattering mechanisms such as phonon scattering and ionized impurity scattering, resulting in decreased mobility. A lattice structure which is distorted too much in this way can no longer be effective either in generating Sn⁴⁺ ions on the substitutional sites of In³⁺ or in generating effective oxygen vacancies. The range of SnO₂ concentration of 4-6 wt% gives a minimum resistivity, because, the carrier density Nₑ has a maximum in this level of doping (see Fig.2-2). A carrier density greater than 10⁲¹ cm⁻³ would reflect the contributions from the oxygen vacancies and interstitial indium atom as well as from substitutional Sn⁴⁺ ions. The mobility values decrease gradually at first, then rapidly, and the carrier density decreases rapidly for dopant concentrations of above 5 wt%.

The scattering in the lattice has also been noticed by Muller[26] on sputtered undoped In₂O₃ films. This, in fact, comes from strong disorder given by particular structure of In₂O₃. It was observed that characteristic behaviour of semiconductors with low mobilities is caused by scattering at the charged impurity centre. This existence was also found by Noguchi et.al[27] to account for the observed low mobility and its dependence on the carrier concentration and temperature in reactive evaporated In₂O₃ films. He stated that scattering due to grain boundary is not considered to be important.
Figure 2.2
The dependence of electrical properties of ITO on the content of SnO$_2$ (Ref 15)
Shanthi et. al[21,27], however, discovered that the grain scattering was the dominant mechanism for the case of Sb doped and undoped SnO₂ deposited by the spraying method. This scattering governs the change in the electrical parameters of the films. They also concluded that in Sb doped SnO₂, the oxygen states present at the grain boundaries modulate the barrier height, thereby changing the mobility and resistivity. This is in agreement with the model shown by Anderson[7] and Ling et. al[28] who investigated indium antimonide films deposited by flash evaporation. They claimed that the mobility is very much affected by scattering at the surface and grain boundaries. These surface and boundary effects can play a dominant role in limiting the mobility and determining electrical performance of the films. These are, assumed, to be due to a potential barrier at the boundary.

The approximation made by Anderson[7] is to consider a non-degenerate impurity semiconductor with parabolic bands. This is based on the fact that the surface of a semiconductor will, generally, have dangling bonds which will act as electron traps. As a result of this, an n-type film will have a surface in which the mobile carriers are depleted. This is represented in a band diagram by an upward bending of the conduction and valence band edges. Since each crystallite boundary will also contain dangling bonds there will be a potential barrier for electron in an n-type film.

Figure (2.3) shows a one dimensional diagram of parabolic
Figure 2.3.

The barrier model.
A one dimensional diagram of parabolic bands
(Ref 7)
bands in which \( x \) is an arbitrary direction through the crystal. It is assumed that the donor density is to be \( N_d \text{ m}^{-3} \) and that all donors are ionized \( (n \approx N_d) \) where \( n \) is the mobile carrier density. From the well-known Boltzmann expression, the carrier concentration in the conduction band can be expressed as:

\[
N_d \approx n = N_c \exp \left[ - \frac{E_c - E_F}{kT} \right] \quad \ldots \ldots (2-1)
\]

where the effective density in the conduction band edge is:

\[
N_c = 2 \left( \frac{2\pi m_e kT}{h^2} \right) \quad \ldots \ldots (2-2)
\]

\( E_c \) is the energy electron at the conduction band edge, \( E_F \) is the Fermi energy, \( m_e \) is the effective mass of electron and \( h \) is Planck's constant. The effect of trapping in the grain boundaries can be treated as a reduction of the donor density in the barrier region. Then equation (2-1) can be rewritten as:

\[
n_1 \frac{E_{F1} - E_{F2}}{kT} = \exp \left( \frac{E_{F1} - E_{F2}}{kT} \right) \quad \ldots \ldots (2-3)
\]

The subscript 1 represents the bulk of the crystallite and 2 the grain boundary. Since the Fermi energy must be continuous over
the boundary, the height of the barrier is therefore given by

$$e\phi = E_{F1} - E_{F2} \quad \ldots \ldots \ldots (2-4)$$

\(\phi\) is the barrier height given in electron volt. Thus

$$\phi = \frac{kT}{e} \ln \left( \frac{n_1}{n_2} \right) \quad \ldots \ldots \ldots (2-5)$$

It is proposed that the potential barrier, \(\phi\), can always be calculated to a good approximation using equation (2-5) as long as the degeneracy is not too great, and that the proper statistics and band model are used in the calculation of \(n_1\) and \(n_2\).

The carrier density of \(n_2\), according to the model, remains at the surface of the crystallite. Then it is clear that only those carriers are able to cross intercrystalline boundaries. Therefore, if it is assumed that the applied voltage is small and that the boundary is the dominant limiting feature, conductivity can be written as :-

$$\sigma = n_2 e \mu_B \quad \ldots \ldots \ldots (2-6)$$

where \(\mu_B\) is the mobility due to scattering at the physical grain boundary. This equation neglects the resistivity of the bulk of the crystallite compared with that due to the boundary. Substituting from equation (2-5), then the equation becomes
If normal Hall effect and conductivity measurements are performed, the carrier density and mobility calculated from them will include the effects of the barrier, and it will also include the normal electron mobility $\mu_L$ due to the lattice interactions. In a polycrystalline film, however, the mobility is generally much lower from the bulk value, and it can be assumed that $\mu_B \ll \mu_L$. Therefore, from equation (2-7), the conductivity mobility is given by:

$$\sigma = n_i e \mu_B \exp\left(\frac{e\phi}{kT}\right) \quad \text{(2-7)}$$

This equation implies that the relation between $\mu$ and $1/T$ should give a straight line over the temperature range where the assumptions given above apply.

2.4. OPTICAL PROPERTIES.

In general, the sources of light loss in transparent conducting films are absorption, reflection and scattering.
Charge absorption, absorption by bound charges and molecular scattering are related to the film materials themselves. The ratio of the transmitted light intensity $I$ to the incident light intensity $I_o$, when light is pass through an absorbing film, is given by the following equation (Lambert's law):

$$\frac{I}{I_o} = e^{-\alpha t} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2-9)$$

where $\alpha$ is the absorption coefficient, and $t$ is the thickness of the film. This law is not acceptable for transparent conducting films since it assumes that no reflection phenomena occur. However, it is acceptable for reviewing absorption\[1\].

The involvement of transparent conducting films in the field of solar cell technology is very important in order to enhance the performance of the device. The transmission required is as wide as possible so that it transmits almost the whole of the solar spectrum. The thickness of the films can be adapted to play the role of a very efficient anti-reflective coating (ARC), as their indices are very close to the square root of the silicon substrate indices ($n_{Si} \approx 3.5-4$). Therefore, such ARC is necessary in order to reduce the reflectivity for silicon, which is high along the solar spectrum, from 30% down to 10%. In addition to this, transparent conducting films can serve the following function\[29\] :

(i) act as an optical window for the base (absorber) semiconductor.
(ii) serve as an electrical conductor for collecting the photocurrent.

(iii) form a potential barrier at the base semiconductor for photovoltaic action.

2.4.1 Absorption.

Charge carrier absorption is the most important mechanism for the case of transparent conducting films. Several mechanisms are known that produce this effect. The only important mechanism, in the case of metals is electron heating by incident photons, and the absorption coefficient $\alpha$ in equation (2-9) is related to one of the optical constant of the relevant metals (the extinction coefficient $k$) by the expression:

$$\alpha = \frac{4\pi k}{\lambda} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (2-10)$$

The most direct method for probing the band structure of semiconductors is to measure the absorption spectrum. In the absorption process, a photon of a known energy excites an electron from a lower to a higher energy state. The fundamental absorption refers to band-to-band or to exciton transitions, i.e. to the excitation of an electron from valence band to conduction band.

Transparent conducting oxide such as In$_2$O, SnO$_2$ and ITO has high optical transparency in the visible and near IR regions of
the solar spectrum. This is an apparent contradiction because the nature of these material is to be insulators due to a wide forbidden band gap (\( E_g \geq 3.0 \ \text{eV} \)). However, they are used as semiconductors. Typical spectra for transmission, \( T \), reflection, \( R \), and absorption, \( A \), of a sprayed ITO film is shown in Fig (2.4) for a given wave length varying from 0.3 to 2.4 \( \mu \text{m} \).

Investigation on optical properties of SnO₂ have been carried out by Kohnke[30]. From the short wavelength cut-off, he found the fundamental optical energy gap, \( E_g \), to be \( \geq 3.54 \ \text{eV} \). Values of \( E_g \) of In₂O₃ film \( \approx 3.75 \ \text{eV} \) have been reported by Weiher et.al[31] from a direct-allowed transition and \( E_g \approx 2,619 \ \text{eV} \) from indirect-forbidden transition. It has been known that for direct (vertical) band-to-band transitions, the energy dependence of the absorption coefficient, \( \alpha \), is of the form

\[
\alpha = \alpha_0 (h\nu - E_g)^x
\]  

(2-11)

where \( h\nu \) is the photon energy, \( E_g \) is the energy band gap and \( \alpha_0 \) is a constant. The value of \( x \) is \( 1/2 \) for allowed transitions and \( 2/3 \) for forbidden transitions. By plotting the experimental values of \( \alpha^2 \) vs. photon energy, and extrapolating to zero absorption, the width of energy gap may be obtained.

It is assumed by Summitt et.al[32], who also worked on the SnO₂ model, that the lower curve portion of \( \alpha^2 \) vs \( h\nu \) dependence represents the allowed indirect phonon assisted transitions, which could vary as[33,34] :-
Typical spectral of transmission, T, reflection, R, and absorption, A, for an ITO film as a function of wave length. (Ref 43)
\[ \alpha = \alpha_0 \left( \hbar \nu - E_g' \mp E_p \right) \]  

\[ \ldots \ldots (2-12) \]

where \( E_g' \) is the minimum forbidden gap, and \( E_p \) is the phonon energy. When a single phonon frequency is involved, the plot of \( \alpha \) vs photon energy can be extrapolated to \( E_g' + E_p \) and \( E_g' + E_p' \) from which one can obtain both \( E_g' \) and \( E_p \). By plotting lower absorption as \( \alpha \) vs photon energy (Fig. 2.5), Summitt et al.\textsuperscript{[34]}, who used polarized radiation light, obtained \( E_g' + E_p = 3.72 \) and \( 3.42 \) eV for parallel and perpendicular gaps respectively. Broadening occurs at the bottom of both sides, but is much larger in the parallel edge. Broadening of the perpendicular edge suggests that several phonon frequencies participate in the absorption.

Kostlin et al.\textsuperscript{[35]} discovered that the free electrons are also affecting the fundamental absorption in the near UV region of the spectrum. In the range of the band absorption, a shift is also to be seen, that is, the higher the free electron density the shorter the wave length of the intrinsic absorption edge (see Fig. 2.6.). They used only one sample, instead of several, to investigate this effect, and this is to eliminate effects of film thickness so that the shift can be accurately recognised. The electron density of the sample is varied by oxidation and reduction. This shifting effect can be interpreted as a Moss-Burstein shift\textsuperscript{[37]}.

To explain this shift the semiconductor needs to be heavily doped\textsuperscript{[36-38]}. The Fermi level is located inside the conduction band.
Figure 2.5

$(\text{Absorption coefficient})^{1/2}$ vs photon energy.
(Ref 34)
Figure 2.6.

The spectral transmission for In$_2$O$_3$: 6 % Sn in the UV band region for different values of electron density (0.4, 0.5, 0.6 and $1.1 \times 10^{21}$ cm$^{-3}$) (Ref 35)
(n-type material). The optical transmission of this degenerate semiconductor involves vertical transitions from the filled band in the valence band to the lowest unfilled level $E_m$ in the conduction band (see Fig. 2.7). The bottom point of conduction-band states are assumed already occupied. The location of the lowest unfilled level $E_m$ is approximately $4kT$ below the Fermi level. Fundamental transitions below $E_m$ are then forbidden, and hence the absorption edge should shift to the higher state. Since $E_m$ has become the lowest usable state of the conduction band, then $E_F - E_c = 4kT$ at an electron density value of $N_m = 1.0 \times 10^{18}$ cm$^{-3}$. The optical energy $E_o$ should therefore be equal to $E_g$ ($E_o = E_g$) for electron density smaller than $N_m$ ($N < N_m$). In the case of degenerate semiconductors the electron density is bigger than $N_m$ ($N > N_m$), and therefore, the optical energy $E_o$ is approximately equal to:

$$E_o = E_g + (1 + \frac{m_e}{m_h}) \left( E_F - E_c - 4kT \right) \quad (2-13)$$

The last part of the equation above is known as the shift, where $m_e$ and $m_h$ are electron and hole mass respectively, and $E_g$ is the energy band gap. The shift in the optical absorption edge toward higher energy with an increase in the carrier concentration has also been found by other researchers$^{[42-45]}$.

Another phenomenon frequently observed in the direct transitions between bands is absorption tails$^{[26,31,36]}$. Urbach's rule can be fitted to a band structure having exponential tailing into the forbidden energy gap due to the presence of a substantial
Figure 2.7

Shift mechanism in the parabolic band.
(Ref 37)
number of ionised impurities. These impurities exist at energy levels within a few kT of either of the two bands.

At low densities, shallow impurities form discrete localised energy levels in the forbidden gap. If the impurity concentration is increased sufficiently, the impurity wave functions overlap, forming an impurity band in which the electrons or holes are free to move. At still higher concentrations, the impurity bands broaden, eventually to overlap the main band edge and form a density-of-states tail which extends into the forbidden gap. The precise doping levels at which overlap occurs are uncertain. This is because the impurities are distributed in a random fashion throughout the lattice and this has the effect of increasing the width of the impurity band\textsuperscript{[39]}\textsuperscript{.} The assumption of the distribution of impurities quoted by Stern et al\textsuperscript{[40]} is \(N_{\text{min}} \approx 3 \times 10^{23} \left(\frac{m^*}{m_e \epsilon}\right)^3 \text{ cm}^{-3}\) which is the concentration at which overlap with the main band takes place. \(m^*\) is the effective mass of the carrier in the main band and \(\epsilon\) is the dielectric constant of the material.

In absorption, the effect of the band tail is usually masked by the Burstein-Moss shift of the absorption edge to larger energies. In order to observe optical transitions to states within the tail, it is necessary to add a sufficient number of compensating impurities to deplete the tail states. If the acceptor concentration is just sufficient to compensate for the donors, the strongest optical transitions will be initiated from the top of the valence band, and an absorption tail will be observed which falls off with wave length at a rate determined
primarily by the density of states in the donor tail. As the acceptor concentration is increased further so that the Fermi energy is shifted into the valence band, a Burstein-Moss shift to a larger energies will be observed, but the shape of the absorption tail will still be determined mainly by the conduction-band tail states. Figure (2.8) shows the shift due to exponentially increasing absorption edge which is observed by Pankove\textsuperscript{[38,41]} in GaAs material which illustrates how absorption probes the conduction band tail states in a p-type semiconductor.

Investigation done by Muller\textsuperscript{[26]}, on In\textsubscript{2}O\textsubscript{3} films deposited by reactive sputtering, shows a considerable absorption tail at low photon energies ($h\nu < 3.7$ eV) which is not caused by indirect interband transitions. He stated that an exponential decrease of such absorption tails is analogous to Urbach's rule. The causes of such absorption tails are ascribed to lattice imperfections\textsuperscript{[59]}, that is, defect terms near the band edges (band tailing) or statistical variations of the energy gap due to local lattice deformation\textsuperscript{[41]}, which may result from statistical variations to the concentration of defects.

\textbf{2.4.2. Transmission.}

The average transmission of the conducting oxide films is between 80 and 90\% up to a region where free carrier absorption begins. The variations of transmission are mainly due to interference phenomena. The index of refraction of the substrates
Figure 2.8.

Energy diagram illustrating how absorption probes the conduction band tail of states.

(Ref 38)
is mostly around \( n = 1.5 \) and since the layers have relatively high indices \( (n \approx 2) \), reflection is then the main source of loss. At a minimum of transmission and for normal incidence of the impinging light, the transmission can be written as:

\[
T_{\text{min}} = \frac{4 n_f^2 n_s}{(n_f^2 + n_s)^2} \quad \ldots \quad (2-14)
\]

\( n_f \) and \( n_s \) are being the film and the substrate indices respectively. The value of \( n_f \) can be deduced for the wavelength at the minimum of transmission \( T_{\text{min}} \):

\[
n_f = \left[ \frac{n_s(2 - T_{\text{min}}) + 2n_s(1 - T_{\text{min}}) \frac{1}{2}}{T_{\text{min}}} \right]^{\frac{1}{2}} \quad \ldots \quad (2-15)
\]

The calculated \( n_f \) value from the equation above can be used for evaluating the thickness, \( t \), of the layer by using the pattern of transmission with successive minima and maxima and using the following equation:

\[
t = \frac{M \lambda_1 \lambda_2}{2 \left[ n_f(\lambda_1) - n_f(\lambda_2) \right]} \quad \ldots \quad (2-16)
\]
where $M$ is the number of oscillations between the two extrema occurring at $\lambda_1$ and $\lambda_2$, $n_1(\lambda_1)$ and $n_1(\lambda_2)$ being the corresponding refractive indices.

In the near IR region of band spectrum, when the free carrier absorption becomes important, the permittivity and the absorption coefficient $\alpha$ can be written\textsuperscript{1,46-48}:

\begin{equation}
\epsilon = \epsilon_L - \frac{N q^2}{m_e \omega^2} \quad \ldots \ldots \ldots (2-17)
\end{equation}

and

\begin{equation}
\alpha = \frac{N \lambda_o ^2 q^2}{4 \pi^2 \epsilon_o m_e c^2 n_1 \mu_e} \frac{1}{\langle \tau \rangle \langle \tau \rangle} \quad \ldots \ldots (2-18)
\end{equation}

where $\lambda_o$ is the free space wavelength, $N$ is the free carrier density, $\mu_e$ is the mobility, $m_e$ is the conductivity effective mass and $c$ is the speed of light in vacuum and $\omega$ is the plasma oscillation frequency. $\epsilon_L$ is the contribution to the permittivity due to the polarisation of the atom in the lattice. $\tau(E)$ is the mean free time between collision (relaxation time) for a free electron of energy $E$ and $\langle \tau \rangle$ is the mean value of $\tau$ integrated over the allowed electron energies. The assumption made for the equation above is that $\omega \langle \tau \rangle \gg 1$, where the condition holds in the near IR of the spectrum. It can be seen from equation (2-18) that
the absorption coefficient $\alpha$ is proportional to carrier density $N$, the square of the free space wavelength $\lambda_0$ and inversely proportional to the mobility.

At the condition of $\omega < r > \approx 1$, the optical properties of the films can also be characterized by plasma oscillation, $\omega_p$, of free carriers. This value can be obtained from equation (2-17) with $\epsilon_0$ equal to zero. This is of special interest because the frequency $\omega_p$ is given by:

$$\omega_p = \frac{q^2 N}{m_e \epsilon_L} \quad \text{.........(2-20)}$$

Equation (2-2) gives the oscillation frequency at which an undamped plasma of electrons and positive ions will be oscillate as a whole. Under this condition, equation (2-17) yields the plasma wavelength $\lambda_p$ as:

$$\lambda_p = 2\pi c \left( \frac{m_e \epsilon_L}{q^2 N} \right) \quad \text{.........(2-21)}$$

For wavelengths larger than $\lambda_p$, $\epsilon$ in equation (2-17) is negative, hence, the plasma becomes reflective. This is the onset of the highly reflecting IR region of the films. The condition of $\omega < r >$
> 1 is fulfilled for SnO₂ and ITO layers and the reflection and transmission spectra can be fitted using this model\(^1,14,33\).

### 2.5. STRUCTURES AND PROPERTIES OF SOME SEMICONDUCTING OXIDE FILMS.

#### 2.5.1. Tin Oxide (SnO₂).

Thin conducting oxide films have been claimed to be amorphous\(^49,52\), polycrystalline\(^60,81\) and single crystal\(^37,53\). The nature of these films is mostly polycrystalline and depends on the method and conditions of preparation. The size of crystallites varies from less than a few nanometres, which is considered to be amorphous, to several hundred nanometres. These size variations, of course, affect some of the electrical properties such as mobility and resistivity\(^1\). Manifacier et al.\(^1,43,46\) used a spraying method for depositing In₂O₃, SnO₂, and the mixture of them, i.e. ITO, and obtained crystal structures which were polycrystalline when the films were deposited between the range of temperatures of 350 to 550 °C.

The variation of the grain size deposited by reactive evaporation was also reported by Muranaka et al.\(^52\) to be 70 – 100 nm. They discovered that the crystalline phase of the SnO₂ films was dependent on the oxygen pressure and substrate temperature. Films that were deposited at higher oxygen pressure of 1 x 10⁻² Torr and at substrate temperature of 250 °C have been found to be amorphous. At oxygen pressure of 1 x 10⁻³ Torr, the substrate
temperature had a marked effect on the crystallinity of films. Amorphous films were found at temperatures below 300 °C and crystalline films were formed at temperature above about 350 °C. They claimed that the best crystalline films were obtained at pressure of $3 - 5 \times 10^{-3}$ Torr and temperature of 420 °C. In this particular condition, they possess good transparencies and low resistivities.

The range of grain size for SnO$_2$ films deposited by the CVD method is found to be 7 - 15 nm for film thickness 50 - 100 nm$^{[51]}$. Shanthi et.al$^{[27]}$ found that the grain size of SnO$_2$ was around 25 nm for the films deposited by a spraying method. The grain size increases to 60 nm on addition of antimony. Studies done by Grosse et.al$^{[46]}$, for the same material, showed that the grain size increases with the film thickness in samples prepared at the same temperature. Therefore, they concluded that the grain size is typically of the order of the film thickness.

The diffraction pattern of SnO$_2$ film deposited by CVD, which is shown by Sundaram and Baghawat$^{[50]}$, indicates that the films deposited at low temperature ($\approx 350$ °C) possess fewer intensity peaks (see Fig 2-9). The peaks are (110), (101), (200), (211), whereas the films which are deposited at high temperatures (450 and 550 °C) showed more peaks (sometimes up to as many as seven). Since all the peaks are sharp, it is evident that the films deposited at low temperatures are polycrystalline in nature, but they could have some amorphous background if deposited even lower temperatures ($\leq 350$ °C). While the films deposited at higher
Figure 2.9

X-ray diffraction pattern for SnO₂ films
(a) deposited at 350 °C, (b) deposited at 400 °C.
(Ref 50).
temperatures (≥ 350 °C) showed the maximum intensity for the (110) and (101) plane at temperature deposition of 350 and 450 °C respectively, and showed a maximum for the (211) plane for the films deposited at temperatures 450 and 550 °C. All of the peaks can be explained in terms of preferential orientation of the planes; as the deposition takes place, depending on the temperature being applied, some of the planes orientate themselves to give maximum reflection. It is pointed out by Sundaram et. al[50] that the various planes could be estimated by measuring the peak heights directly on the diffractometer chart, and they concluded that the films deposited at higher temperature have better crystallinity and grain size. This is drawn from the fact that as deposition temperature increases, the intensity peaks increase.

The existence of preferred orientation of the crystallites and its dependence on substrate temperature has also been revealed by Maudes et. al[54] for undoped SnO₂ films. They claimed that the lattice structure is retained as the tetragonal rutile structure of bulk SnO₂. This structure is always consistent for bulk SnO₂ if it is deposited under optimum condition[47,55].

Muranaka et. al[52] also stated that the crystalline SnO₂ films, which were deposited at temperature of 420 °C, are mainly composed of the rutile-like SnO₂ which is similar to the bulk nature of the SnO₂ if they are deposited under optimum condition[1,47,55]. The unit cell is, in fact, tetragonal with the well-known rutile structure of TiO₂, containing six atoms, two tin (Sn) and four oxygen (see
Fig. 2-10). The lattice parameters are $a = b = 4.737 \, \text{Å} \text{ and } c = 3.185 \, \text{Å}$ \cite{1,2,47,52,55}. It is generally agreed that SnO$_2$ is an extrinsic (defect) semiconductor, and that pertinent electrical properties depend strongly on stochiometry. As reported by Kohnke\cite{50}, the SnO$_2$ crystals are not very pure and have a high dislocation density. He found the fundamental bandgap $\approx 3.54 \, \text{eV}$, a sharp absorption peak at $\lambda = 3.07 \, \mu\text{m}$ (attributed O-H groups in the crystal), carrier concentrations from $10^{14} - 10^{15} \, \text{cm}^{-3}$, Hall mobility varies from $10 - 300 \, \text{cm}^2 \, \text{V}^{-1} \, \text{sec}^{-1}$, donor densities about $10^{20} \, \text{cm}^{-3}$ and a donor activation energy of about 0.7 eV.

2.5.2. Indium Oxide (In$_2$O$_3$).

The structure of indium oxide films are more complicated than tin oxide. They are generally polycrystal with a cubic bixbyite structure\cite{2,15,47,56-58} in the bulk material and with little change in the lattice parameter (the lattice constant $a = 10.118 \, \text{Å}$). Investigation done by Nath et al\cite{57} on In$_2$O$_3$ and In$_2$O$_3$(Sn) films, deposited by reactive evaporation, revealed a similar structure for both of them. In$_2$O$_3$(Sn) films exhibit a (111) preferred orientation, whereas pure In$_2$O$_3$ films show a (100) direction.

A similar method was also used by Noguchi et al\cite{25} for depositing this film. They discovered that the films were amorphous when deposited at a temperature lower than 100 °C since they gave no observed diffraction peaks. At a higher temperature, however, the films became polycrystalline; this crystalline structure was detected based on one weak diffraction peak
Figure 2.10 (a)
Crystal structure of SnO\textsubscript{2} large circles indicate oxygen atoms and the small circles indicate tin atoms. (Ref 55)

Figure 2.10 (b)
The In\textsubscript{2}O\textsubscript{3} unit cell showing the positions of the indium atoms and two of the distorted oxygen octahedra (Ref 62,63)
indicating (222) orientation. They also found that the low temperature deposited films consisted of fine-grained crystallites which might be incompletely oxidised indium oxide with non-stoichiometry. Moreover, the grain size in the film became larger as the temperature increased.

The degree of orientation of the sputtered In$_2$O$_3$ texture has been stated inclusively by Lehman et al.\textsuperscript{[68]} and Fan et al.\textsuperscript{[14]} to be (111) orientation when it is sputtered slowly (\(\approx 100 \text{ Å/min}\)) and at relatively low pressures (\(\approx 5 \text{ mTorr}\)). If the films are sputtered at high rates (\(\approx 500 \text{ Å/min}\)) and high pressures (\(\approx 20 \text{ mTorr}\)), they become partially amorphous and show only some weak preferred (111) and (110) orientation. X-ray diffraction patterns of In$_2$O$_3$ deposited by thermal evaporation\textsuperscript{[51]} is shown in Fig. 2-11. The films were deposited at a temperature of below 150 °C and afterward they were heat treated in air at a temperature of 500 °C. The intensity peak of the In$_2$O$_3$ powder sample shows (222) orientation. These films have also been deposited on quartz and glass substrates. The relative intensity of the diffraction pattern for these films are equal to randomly orientated powder patterns, ie.(222). This indicates there is no preferential orientation in these In$_2$O$_3$ films. The grain size observed for the film deposited by this method is around 3 - 10 nm\textsuperscript{[51]}

Single crystal of In$_2$O$_3$ films have been reported by Weiher et al.\textsuperscript{[31,53]}. They grew single crystals of indium oxide from the vapour phase of indium metal and ambient oxygen, and heated it in a furnace at a temperature of 1000 °C for 24 hours. An x-ray
Figure 2.11.

X-ray diffraction pattern for In$_2$O$_3$ films
(a) powder sample, (b) deposited on quartz glass
(Ref 51)
identification shows square and hexagonal cross-section growth in the (100) and (111) crystal directions. Bandgaps have been found to be 3.75 eV in direct transition and 2.619 eV in indirect transition. The electrical conductivity at room temperature is the order 10 Ωcm⁻¹ and the mobility is approximately 160 cm² V⁻sec⁻¹. The temperature dependence of the mobility has been quantitatively interpreted in terms of lattice and ionized scattering, and the donor ionization energy has been found to decrease with increasing impurity concentrations. High apparent intrinsic conductivity with an activation energy of 1.55 eV has been observed at elevated temperatures.

2.5.3. Tin Doped Indium Oxide (ITO).

The structure of indium tin oxide films (ITO) retains the bulk structure of In₂O₃, but exhibits a slight increase in the lattice constant (10.118 Å < a < 10.31 Å)\(^{[13,49,58,59]}\). This slight increase has been found to depend on the deposition conditions and parameters\(^{[13,59]}\). Typical grain size ranges have been claimed by Steckl et.al\(^{[17]}\) to be 40 - 60 nm for the films deposited by sputtering. From x-ray data, there was no evidence of crystallinity observed for the as-deposited films and annealed films at low temperature (≤ 100 °C). The crystal orientation was observed only for the films which are annealed at high range temperature of 300 - 500 °C and the orientation observed was in the (222) direction.
ITO films deposited by the spraying method have been discovered by Kulaszewicz\textsuperscript{[49]} to be amorphous at lower spraying temperatures ($\approx 673$ K). It was found that the film started to crystallize when the temperature was increased and the lattice constants increased linearly with temperature. The films sprayed at temperatures of $823 - 973$ K were crystalline with a cubic pattern. Similar results have also been described by Itoyama\textsuperscript{[60]} who deposited the films using sputtering. He found amorphous-like structures in the as-deposited films. He suggested that crystallisation is inhibited in low temperature substrates due to mobility-reducing, and consequently, the films are highly disordered, amorphous-like states. The amorphous-like films can be easily transformed to crystalline states by heat treatment.

The diffraction patterns of annealed ITO films, made by Itoyama, exhibit only the $\text{In}_2\text{O}_3$ peaks, and the peaks of $\text{SnO}_2$ and $\text{Sn}_3\text{O}_4$ were very weak. The annealed films deposited at low deposition rates ($< 2000 \text{ Å/min}$) shows the (400) peak is the most prominent. All other peaks other than (400) are either weak or absent. This indicates that the films have strong (100) texture. At higher deposition rates (over $3000 \text{ Å/min}$), the (222) is the most prominent peak, indicating the existence of (111) texture. These results show that the crystal structure of heat-treated films is transformed from (100) to (111) orientation with increase in the deposition rate, and suggests that the crystalline growth starts from nucleation centres possibly produced during deposition\textsuperscript{[2,60]}. The difference in the orientation has also been stated by Frasser\textsuperscript{[61]} due to variation of substrate temperatures.
The possible conductivity of these films, generally, involve oxygen deficiencies during either the film growth or annealing of the films. The conductivity is increasing with tin doping in the film\[2,13-18,47\], and the typical carrier density of these films is \( N \approx 10^{21} \text{ cm}^{-3} \), mobility \( \mu = 15 - 40 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \), leading to resistivity range of \( \rho \) from \( 7 \times 10^{-5} \) to \( 5 \times 10^{-4} \, \Omega \text{cm} \). The direct optical gap has been claimed to be around \( 3.75 \, \text{eV} \)[47] and the refractive index in the visible band exhibits a marked scatter between \( 1.8 - 2.1 \)[14,22,48].

2.6. SUMMARY.

A survey on the physical, electrical, optical and structural properties of semiconducting oxide materials has been given. Some transparent semiconducting films, which are the nearest to the material used in the experiment, have been surveyed. Possible conduction mechanisms in these oxide films are discussed by a non-stoichiometry (oxygen deficient), addition of impurities (substitutional or interstitial) and the valency difference in the constituents of the lattice.

The electrical properties of the semiconducting oxide films are generally dependent on composition, thickness and temperature ambient during deposition or post deposition. Film composition is determined by the concentration of impurity additions in the compounds. The impurity concentration alters the electrical properties of the materials\[5,13,18\]. High substrate temperatures during deposition of Sn doped In\(_2\)O\(_3\) decreases the resistivity\[14\].
However, carrier concentration and Hall mobility are increased with increasing temperature. Annealing of the film after deposition was observed by Steckl et al.\[17\]. For films annealed at low temperature (\( \approx 200{^\circ}C \)), it was found that the properties of the film were improved, but degradation occurred at a higher annealing temperature.

The optical property is one of the important factors since the knowledge of the transparency of the film is required for application to solar cells. Losses of light in transparent conducting films are generally due to absorption, reflection and scattering. Charge carrier absorption is the most important mechanism in the case of these films. By measuring the absorption spectrum, the band structure of oxide semiconductors can be traced. A review of investigations on optical properties for some semiconducting oxides has been given.

The structure and properties of some related semiconductor oxide films (ie. SnO\(_2\), In\(_2\)O\(_3\) and ITO) have been reviewed. The nature of these films is polycrystalline. The crystal size varies depending on the methods and conditions of preparation. Some studies from other researchers have been written about in this chapter.
REFERENCES


3.1. TECHNICAL REVIEW.

The development of photovoltaic cells, or solar cells, can be traced back from the discovery by Becquerel (1839) that a photovoltage resulted from the action of light on an electrode in electrolyte solution[1]. This discovery was continuously developed until the modern era of photovoltaics began in 1954 where solar cell conversion efficiency of 6% was reported by Chapin et.al[2] using silicon single-crystal wafer. With improved technology, silicon cell technology had reached 14% efficiency under terrestrial sunlight in the early 1960's.

The basic principle of solar cells is receiving energy supply in the form of photons from the solar spectrum and producing usable electrical energy. In order to describe the properties and use of photovoltaic solar cells, it is important to consider the sequence of phenomena involved, that is, from the radiation received from the sun, through the processes of absorption of this radiation, generation and transport of charge carriers in the semiconductor, separation of charge carriers by the junction and collection of these carriers at the contacts of the device. For eventual terrestrial use, a photovoltaic generator of electricity must be coupled with an effective storage process in
order to compensate for the intermittent nature of solar radiation.

The electronic description of the solar cell device is based on a model of a diode. This device is composed of three functional elements, namely, an absorber, a junction or converter and a collector. The absorber has the function of absorbing the sunlight spectrum. When the sunlight interacts with the front surface of the solar cell, useful absorption will result in the generation of electron-hole pairs and parasitic absorption resulting in heat. Some power is reflected at the cell surface, and a part of the light is not absorbed but is transmitted through the cell. The generated electron-hole pairs will be separated by a potential barrier in the junction and the electrons will be collected by the n-type and the holes by the p-type region.

Figure 3.1 shows some possibilities of the incident radiation path on the solar cell. The first two points are the transmitted and reflected radiations. The third point is, the photon is absorbed far from the junction; although it generates an electron-hole pair, this will recombine before reaching the potential barrier. Fourthly, the photon which is absorbed creates an electron-hole pair within the diffusion length from the potential barrier, so that, the carriers in this area are separated by an electric field existing across the depletion layer. Thus, the first three points constitute losses in the
Figure 3.1

Incident radiation path on the solar cell. Path 1, 2, 3 are considered to be losses in the energy conversion mechanism.
energy conversion mechanism, and only the last point is useful to generate electrical power.

The absorption properties of solar cell materials determine to a large extent how much of incident radiation can be converted into electricity. The absorption of light in a semiconductor is determined by several mechanisms, of which the two most important are the excitation by a photon of an electron from the valence band to the conduction band and transition within a band. The first mechanism, referred to as the fundamental absorption, uses a photon with a minimum energy at least equal to energy gap $E_g$ of the semiconductor ($E_{ph} \approx E_g$). For a photon with energy much larger than $E_g$ ($E_{ph} \gg E_g$), only one electron-hole pair is generated. The energy excess of $E_g$ being dispersed as thermal energy and thus lost for photovoltaic conversion.

3.1.1. Band model of a solar cell.

The simplest way of explaining the model of a solar cell is by using the homojunction p/n diode, since it is the most understood structure up to date. The material is assumed to be a single crystal semiconductor. The light with energies $E_{ph} \geq E_g$ excites electrons from the valence band to the excited states in the conduction band (see Fig. 3.2), and photogenerated electron-hole pairs are created in the top layer, in the barrier region and in the base layer. The width of the barrier region is very narrow compared with the others (drawing is not to scale), so
Figure 3.2
Band model of a solar cell (a) In equilibrium condition (b) Under illumination.
that, collected photogenerated carriers rely on diffusion from the top and the base regions.

Large electrostatic fields are present in the barrier region only. In this case, the electric field of the barrier region acts as a sink which draws photogenerated holes from the n-type top layer and photogenerated electrons from the p-type base layer. The electrostatic built-in potential $V_D$ will adjust its value such that the statistical diffusion force acting on both carriers is exactly balanced by the electrical force. This leads to the total energy being constant. At thermal equilibrium, electrons diffuse from the n side into the p side to recombine; on the other hand, electrons in the p side will be attracted towards the n side such that the two currents exactly balance. The dependence on the physical parameters of the two currents is completely different. The electron current flowing from the n- to the p-type region strongly depends on the barrier height. Since the electron source is very large (infinite) in the n-type region, only those electrons which have enough energy will be able to diffuse over the built-in potential barrier $V_D$. The fraction of electrons which can overcome a barrier height of $qV_D$ is given by $\exp(-qV_D/kT)$. Thus the current passing from n region to p region is then given by:

$$J_{n \rightarrow p} = Cn_n \exp (- qV_D/kT ) \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (3-1)$$
where $k$ is the Boltzmann constant, $T$ is the temperature and $C$ is a proportionality constant.

The electrons which flow from p region to n region face no barrier, in other words, they can flow "down hill". Then the current from p to n region becomes

$$J_{p->n} = Cn_p$$  \hspace{1cm} (3-2)

where $n_p$ is the density of electrons in the uniform portion of the p-region.

At equilibrium, clearly no net electron current can exist, so that,

$$J_{n->p} = J_{p->n} = j_0$$

or

$$C n_n \exp(-qV_D/kT) = C n_p$$

thus:

$$n_p = n_n \exp(-qV_D/kT)$$  \hspace{1cm} (3-3)

This is an equilibrium ratio of electrons in the n-type and p-type materials. $n_p$ electrons per unit volume of p-type material are minority carriers.

At this point, it is possible to examine the consequences of lowering the barrier height which can be done in two ways. One way is to simply apply a bias voltage across a composite crystal
so that the applied field tends to move electrons from the n-region to the p-region. The other way is to illuminate the crystal, and allow a current to flow in an external circuit. It is the latter phenomenon which is of interest, but it is important to examine the former.

Suppose that the applied bias lowered the barrier by an amount $V$ volts. The barrier height is then $(V_D - V)$ volts, and,

$$J_{n>p} = C_n n \exp\left[-\frac{q(V_D-V)}{kT}\right] \quad \cdots \cdots (3-4)$$

As before, $J_{p>n} = C_p p$, since the barrier height has no effect on the "reverse current". The net current flow is then :-

$$J_e = J_{n>p} - J_{p>n} = J_{es}\left[\exp\left(qV/kT\right) - 1\right] \quad \cdots \cdots (3-5)$$

A similar equation can be derived for holes such that

$$J_h = J_{ho}\left[\exp\left(qV/kT\right) - 1\right] \quad \cdots \cdots (3-6)$$

The total current across the junction is the sum of the electron and hole contribution, that is,
\[ J = J_e + J_h = (J_{e0} + J_{h0}) \left[ \exp \left( \frac{eV}{kT} \right) - 1 \right] \quad \ldots (3-7) \]

It can be seen that the total current on this equation depends strongly on the bias voltage. This is known as a diode equation which shows a rectifying behaviour.

In the case that incident light is used as a bias, then the model can be illustrated as in figure 3.3. In this model, a thin p-type material is joined to an n-type base material. It is assumed an electrical load, \( R_L \), is connected across the two layers and a series resistance, \( R_s \), is included to account for the resistance of the very thin p-layer (Fig 3.3a). As already mentioned, electron-hole pairs are produced in the neighbourhood of the junction and these pairs diffuse to the junction, where a charge separation takes place. It is noted that minority carriers are free to move across the junction and the total minority current across the junction is defined by \( I_s \). These carriers are important in the photovoltaic effect since they are responsible for generating electric currents.

If there is no electrical connection between p and n-type materials, ie. \( R_s \) is unconnected (Fig 3.3b), then it follows that a potential \( V \) must be developed across the junction which push an equal and opposite current in the "forward" direction, since the net current must be zero. This forward current is identical to that which would be obtained by placing the bias voltage \( V \) across
Figure 3.3

Equivalent circuits of the solar cell.
the p-n junction in a forward direction. Therefore, equation (3-7) may be used and, allowing for the fact that it is now using total currents instead of current densities, can be written as:

\[ I_j = I_L = I_o \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right] \] .............................(3-8)

where \( I_L \) is the total minority carrier current across the junction in "reverse" direction, also referred to as "short-circuit current" or "light generated current"; \( I_j \) is the total forward current, also referred to as a junction current; \( V \) is the voltage developed across the junction in a "forward" direction; and \( I_o \) is the reverse saturated current. From the equation above, the series resistance, \( R_s \), is neglected.

Since the model is a generator under open-circuit conditions, the voltage, \( V \), in the equation (3-8), is clearly the maximum attainable voltage which is commonly called "open-circuit voltage", \( V_{oc} \). Then, from that equation, it can be solved to obtain:

\[ V_{oc} = \frac{kT}{q} \ln \left( \frac{I_L}{I_o} + 1 \right) \] .............................(3-9)

If the load across the cell is connected, as in figure 3-3c, then a current may flow in the circuit. The voltage which must be developed across the junction may now be smaller than \( V_{oc} \) to
maintain steady-state conditions; since a smaller forward current is now required. The current through the load will be the difference between the reverse current, which is still the same as under open-circuit conditions, and the new, smaller, forward currents, and is written as :-

\[ I = I_r - I_L \]

\[ I = I_0 \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right] - I_L \] ...............(3-10)

where \( I \) is the current which is transported to the load, and the sign on the \( I_L \) is negative since it is in the reverse direction.

In practical situations there are factors limiting the performance of the device, such as, ideality factor of the diode, \( n \), series resistance, \( R_s \), and shunt or parallel resistance, \( R_{sh} \) (see figure 3-3d). The ideality factor \( n \), in a theoretical case, is assumed to be 1. The current voltage relationship for a simple diode involving \( R_s \) and \( R_{sh} \) is then written as :-

\[ I = I_0 \left\{ \exp \left[ \frac{q(V-IR_s)}{nkT} \right] - 1 \right\} + \frac{(V-IR_s)}{R_{sh}} \] ...........(3-11)

From the equation above, it can be seen that the major effect of \( R_s \) occurs at high current, whereas the effect of \( R_{sh} \) occurs at a small voltage. If the device is illuminated, the equation (3-11)
3.1.2. The I/V characteristics and fill factor.

The I/V characteristics and fill factor are important parameters in discussing the efficiency of solar cells. These also define the maximum attainable power. Figure 3.4 shows plots representing the characteristic of a solar cell in the dark and under illumination. Some additional quantities are introduced here in order to define the performance of the cell. These include open circuit voltage, $V_{oc}$, short circuit current, $I_{sc}$, the voltage for maximum power, $V_{m}$, and the current for maximum power $I_{m}$.

The portion of the curve in the fourth quadrant is the region of a power generation. The maximum power output is defined by the position of $I_{m}$ and $V_{m}$. Fill factor is the usual parameter for characterizing the output of solar cells. This is a measure of the effective utilization of the power producing capability of a cell. It is defined by:

\[
FF = \frac{V_{m} I_{m}}{V_{oc} I_{sc}} \quad \text{..................} (3-13)
\]
Figure 3.4

Typical ideal characteristics of the solar cell.

Line 1 is a characteristic in the dark condition, and line 2 is under illumination.
The significance of the FF is best seen from an inspection of figure 3.4. Cells of reasonable efficiency, have FF values in the range of 0.7 to 0.85.

It is clear from equation (3-10) that \( I = I_L \) when the cell is short circuited, i.e. \( V_{oc} = 0 \). \( I_L \) in the curve is represented by \( I_{sc} \). The product of \( I_{sc} \) and \( V_{oc} \) represents the power output of an ideal cell in which the internal resistance is vanishingly small. In good solar cells, it is found that the actual I-V curve comes quite close to the outer limits of the rectangle. The fill factor can then be used to express the power which is delivered by the cell as :-

\[
P_m = I_{sc}.V_{oc}.FF \hspace{2cm} \text{(3-14)}
\]

The energy-conversion efficiency, \( \eta \), is then given by :-

\[
\eta = \frac{P_m}{P_{in}} = \frac{I_{sc}.V_{oc}.FF}{P_{in}} \hspace{2cm} \text{(3-15)}
\]

where \( P_{in} \) is the total power of the incident light on the cell.
3.2. OTHER STRUCTURES FOR SOLAR CELLS.

In general, the basis for photovoltaic action in a semiconductor device is an electronic asymmetry in the device structure. There is a wide range of photovoltaic device structural possibilities apart from the homojunction which has been described. The most common types of structures are:

i. Homojunction.

ii. Heterojunction.

iii. Schottky barrier.


Homojunction is a junction between n- and p-type portions of the same material. This junction is the simplest to treat theoretically, since its technology is already matured in the electronic component. This type of junction is widely used in the conventional silicon solar cells. Some of the details regarding its function of generating electricity have been previously described.

3.2.1. Heterojunction.

This is a junction made of two different semiconductors with different in bandgaps. The use of heterojunctions (HJ) expands the semiconductor material possibilities for solar cell devices where those materials are capable of giving acceptable
characteristics of the cell and promise a lower-cost of fabrication. Heterojunctions can be of the isotype variety in the form of n-n or p-p junctions, or they can be of the anisotype variety, i.e. a p-n junction.

To understand how equilibrium is established, an n-type semiconductor with bandgap $E_{g1}$ and p-type semiconductor with a smaller bandgap $E_{g2}$ (see figure 3.5) can be used. Their energies are referred to the same reference, that is, the vacuum level. $W$ is the work-function, or the energy needed to remove an electron situated at the Fermi level from the semiconductor. The work-function, thus, specifies the position of the Fermi level with respect to the vacuum reference level. $\chi$ is the electron affinity, that is, the energy required to remove an electron situated at the minimum of the conduction band. In this example, there are energy levels that are occupied by conduction electrons in material 1 and that are unoccupied in material 2. When the two materials are brought into contact, electrons will move from material 1 to material 2. A potential difference will be built up causing a current in the opposite direction. Equilibrium is reached when the Fermi levels of the two materials are lined up (shown in Fig 3.5b). The built-in potential is equal to $W_2 - W_1$, and is divided over the two materials. The situation of this junction is more complicated than in homojunctions due to the difference in bandgap ($E_g$), electron affinity ($\chi$), and work function ($W$). Therefore, depending on the value of these quantities, there can be discontinuities in the band edges and
Figure 3.5

Schematic diagram of heterojunction structure, on which two semiconductor materials with different bandgap, work function and electron affinity are brought into contact.
there can even be a spike as shown in Figure 3.5b. This spike reduces the current from material 2 to material 1 and will thus reduce the short circuit current. Such spikes can be avoided by a proper choice of doping levels and of electron affinities[^4,^5].

In the application of generating electricity by means of photovoltaic effect, light with energy less than $E_{g1}$ but greater than $E_{g2}$ goes through the first material and is then absorbed by the second material. The carriers generated within a diffusion length of the junction or in the depletion region of material 2 are collected exactly as in a p-n homojunction cell. The first material acts as a window for light with energy less than $E_{g1}$. Light with energy greater than $E_{g1}$ will be absorbed by material 1 and carriers generated within a diffusion length from the junction or in the depletion region of material 1 will also be collected.

The diffusion potential of the p-n heterojunction shown in figure 3.5 is given by :-

$$V_D = W_2 - W_1 = E_{g2} - (E_{F2} - E_{v2}) - (E_{F1} - E_{c1}) + (x_2 - x_1) \ldots (3-16)$$

In comparison with the homojunction, $V_D$ can be larger than the width of the small bandgap $E_{g2}$ by an amount of $x_2 - x_1$, that is, the difference in electron affinity of the two materials. Because of the spike in the conduction band edge, the photocurrent will however be smaller than in a homojunction, therefore, it can be
shown that the output power can never be larger than in a homojunction made from either of the two materials.

The potential advantages of a heterojunction for the application of solar cells are as follows:

(i) An enhanced short wavelength spectral response is possible if $E_{g2}$ is so large that the high energy photons are only absorbed in the depletion region of the second material, where collection is very efficient.

(ii) If the first material is highly doped and sufficiently thick without affecting the light transition characteristics, the series resistance can be made very low and the radiation tolerance will be high.

It is also important that, in general, the lattice constants of the two semiconductors are different. This lattice mismatch causes interface states and defects, which can act as recombination centres. The reduced life-time within and around the depletion region increases the recombination and reduces the collection of the photogenerated carriers.

When the band discontinuities are small, and when there are negligible interface traps, calculation of the photocurrents can be made in a similar manner as for silicon p-n homojunction. The reflection of the light at the interface due to the differences of the refractive indices is usually rather small[6,7] and is
therefore often neglected. The spectral response can thus also be calculated in a similar way to that of homojunction. The long wavelength cut-off is now determined by the small energy gap $E_g$ and the short wavelength response by the thickness and the energy gap of semiconductor 1, $E_{g1}$.

The dark current in heterojunctions has several components. These are minority carrier injection from two sides of the junction, recombination in the space-charge region, and tunnelling. The last two components depend on the interface properties of the junction and are only small for a perfect junction. The dark saturation current density, therefore, is usually larger than in a homojunction.

3.2.2. Schottky Barrier.

A Schottky barrier is a metal semiconductor junction. The utilization of this junction is attractive due to apparent simplicity the applicability to thin film polycrystalline materials and the promise of relatively inexpensive processing technology.

When a metal and semiconductor are brought into contact, a potential drop occurs in the interfacial region to account for work function differences, as in the case of the semiconductor hetero-junction. This potential drop occurs in the semiconductor side of the junction (see Figure.3.6) due to differences in the
Figure 3.6

Energy band diagram of metal–semiconductor heterojunction which is known as Schottky–barrier. (a) at zero bias, (b) in forward bias and (c) in reverse bias.
availability of charge carriers in the metal and semiconductor. This can give rise to a depletion region at the interface as in the p-n junction. The metal acts as a heavily doped semiconductor.

The metal-semiconductors, with such a depletion region, have both rectifying and photovoltaic properties. The situation for minority carriers in the semiconductor region is generally the same as for the case of a p-n diode. The excess minority-carrier concentration at the edge of the depletion region, in the dark condition, depends exponentially on the applied voltage, with an exponential decay into the bulk. Minority carrier flows give similar contribution to the total diode current. The only resistance to majority carrier flow between the metal and semiconductor is the depletion-region potential barrier at the interface. The height of this barrier varies with applied voltage as shown in figure 3.6b,c. This gives rise to a thermionic emission component of current given by:

\[
J_{0e} = A' T^2 e^{-q\phi_b/kT} \left( e^{qV/kT} - 1 \right) \quad \text{(3-17)}
\]

where \( A' \) is the Richardson constant (\( \approx 30 \) to \( 120 \) A/cm\(^2\)/K\(^2\)). The magnitude of this component depends on the height of the barrier at the interface (\( \phi_b \)) and the majority-carrier component is normally much larger than the minority-carrier component of current. This extra component of current is undesirable for photovoltaic energy conversion, because it acts to increase the
dark saturation current of the diode and hence decrease the open
circuit voltage. As a result of this, the conversion efficiency of
this device is somewhat lower than the p-n homojunction device,
even though the short-circuit current density can be the same.

3.2.3. MIS/SIS Heterostructure.

Metal-insulator-semiconductor (MIS) and semiconductor-
insulator-semiconductor (SIS) structures are very similar to the
two other structure of junctions, already described previously,
except for the insertion of an insulator in between the two
materials in the structure. It is quite probable that most
Schottky barriers include a very thin, or at least several atomic
layers of insulating material introduced unintentionally during or
before fabrication.

Incorporation of a purposely grown thin, insulating layer
between the metal and the semiconductor in a Schottky diode
structure, which then becomes an MIS structure, however, can have
an advantageous effect of increasing the open circuit voltage ($V_{oc}$)
without appreciably decreasing the short-circuit current density
($J_{sc}$) and fill factor (FF)$^{[8,9]}$. The thickness of the effective
insulating layer is generally between 10 – 30 Å$^{[10,11]}$. If the
thickness of the layer is less than 10 Å, the Schottky diode will
retain its original characteristics and the behaviour of the MIS
will not happen. However, in thicknesses above 30 Å, the behaviour
of the MIS device will start to degrade and a strong reduction of
J_\text{sc} and FF becomes inevitable. The insertion of an insulating layer is also applicable to the semiconductor-semiconductor heterojunction resulting in SIS structure.

(a) MIS Devices.

It is known that in the Schottky barrier, the dark saturation current is dominated by the thermionic current corresponding to the majority carrier transport over the barrier. This leads to a decrease of the $V_{oc}$ which indicates a low barrier height in the device. The addition of an intervening insulating layer can reduce the majority carrier transport toward a level comparable to that of the minority carrier component, resulting in a substantial increase in $V_{oc}$ \cite{12,14} due to increase the majority-carrier thermionic emission barrier height $\phi_b$. The increase of the $\phi_b$ is due to the addition of a proper insulating layer, because, the Fermi level is not pinned anymore as in the Schottky barrier device, but it depends strongly on the metal work-function. Since the photogenerated minority carriers must tunnel through this layer, the thickness of the insulating layer must not be thicker than 30 Å in order to maintain high quantum efficiency \cite{15,16}.

Experiment results that have been reported both for M-S (Schottky barrier) and MIS solar cells show that the M-S cells give poorer efficiencies. The best reported efficiency of M-S solar cells for Au/n-GaAs solar cells is 10\% using single crystal GaAs \cite{17}. In the MIS configuration, the same single crystal GaAs
yields efficiencies of 17%\textsuperscript{[18]} due to partial suppression of the majority-carrier current over the barrier height. This configuration has also been successful with both n- and p-type silicon. Cells with efficiencies over 13% have been produced on single-crystal materials\textsuperscript{[19,20]} and high $V_{oc}$ value attained on p-type silicon.

The schematic energy band diagram of MIS structure is shown in figure 3.7. The key parameters of this diagram are the potential barrier heights $\phi_m$ and $\phi_i$\textsuperscript{[21,22]}. The energy difference between the silicon semiconductor and SiO$_2$ insulator conduction band edges ($E_{ci}$ and $E_{cs}$) is $\phi_i = 3.2$ eV. The metal-to-insulator barrier height for the Al-SiO$_2$ combination is $\phi_m = 3.2$ eV. This value is related to the vacuum work function of the metal and it changes for different metals. It also controls the degree of inversion of the base semiconductor. To invert the surface of a p-type base semiconductor to n-type requires $\phi_m$ or $\phi_i$ (for oxide semiconductor) to be low in value. A high value will accumulate, on the surface, more p-type or p$^+$. 

If the value of $\phi_m$ is low, then the dominant tunnel current flow near zero bias is between the metal and the conduction band. This is referred to as a minority carrier tunnel MIS diode. Conversely, if the $\phi_m$ is high, then the surface of the base semiconductor will accumulate and the dominant current is by majority carrier. This is referred to as a majority carrier tunnel diode which is not useful for photovoltaic conversion. It is the
Figure 3.7

(a) Simple energy band diagram of the MIS solar cell.
(b) Possible current transport of p-Si based MIS junction.
minority carrier diode that is the most useful for solar cells.

The possible dark current mechanism in MIS (p-type semiconductor) diode is illustrated in figure 3.7b, and the total dark current is given by

$$J_D = J_{th} + J_{rg} + J_d + J_s$$

(3-18)

where $J_{th}$ is the thermionic current of holes into metal, $J_{rg}$ is the depletion layer recombination-generation current density, $J_d$ is the injection-diffusion, and $J_s$ represents the surface state current density due to charge exchange between the metal and semiconductor band edges via surface states. As already mentioned, the insulating layer will reduce the majority carrier transport ($J_{th}$), which is the biggest portion, comparable to that of the minority carrier components of $J_{rg}$ and $J_d$.

(b) SIS Devices.

Solar cells, historically, have been dominated by silicon p-n homojunction diodes. Extensive investigations of other junctions have been of interest in order to reduce the production cost of those conventional solar cells. Many heterojunctions have been explored as a possible candidate for large terrestrial application. A particular class of heterojunction diodes, namely, the oxide-semiconductor/base-semiconductor have received wide attention. This particular junction is then developed to become an SIS
heterostructure. The advantages of using oxide semiconductors as a window layer is that they are transparent, degenerate and mostly stable under typical environmental conditions. Moreover, they can be deposited at low temperatures, so that, interdiffusion due to high temperature can be minimized.

It is known that in heterojunction configurations crystal structure, lattice constant and thermal expansion should be chosen and matched carefully to obtain a good photovoltaic device. A study made by Schewchun and Singh\textsuperscript{[21,28]} of the materials, reveals that there is no such combination of base-semiconductor and oxide-semiconductor that is particularly compatible. Thus there is no combination likely to form good devices. However, some reports in the literature, have indicated good performance of heterojunction devices while others have not\textsuperscript{[22-25]}. Indium oxide (In\textsubscript{2}O\textsubscript{3}), tin oxide (SnO\textsubscript{2}) and indium tin oxide (ITO) are the common oxide-semiconductors being investigated in this structure.

In examining the available experimental data, it became apparent that the performance of such devices would be dramatically modified as thin interfacial layers or insulators are introduced between the two materials. These insulators are not just simply SiO\textsubscript{2} but they can be complicated mixtures. They appear capable, in some way, of accommodating the strains due to crystal structures, lattice parameters, and perhaps thermal-expansion coefficient mismatch. The incorporation of these interfacial layers in the oxide-semiconductor/base-semiconductor systems results in a
semiconductor-insulator-semiconductor (SIS) configuration. The exact nature of these insulators on either side of the interfacial layer, however, is not entirely understood.

The operation of SIS solar cells is similar to the metal-insulator-semiconductor (MIS) solar cells where the metal is replaced by a degenerate wide-bandgap oxide semiconductor. The difference between the MIS and the SIS is that the oxide semiconductor, which is transparent, has a wide bandgap ($\approx 3.6$ eV) whereas the metal has the property of a variable bandgap which can be set at any value from zero to several electron volts\textsuperscript{[21]. Another substantial difference is that, the MIS diode generally requires about 50 Å of metal thickness in order for it to be sufficiently transparent. Such layers are fragile, easy to oxidize, difficult to make continuous and suffer from high resistance. Oxide semiconductors can approach metallic behaviour ($\approx 10^{-4} \Omega\text{-cm}$), but in layer thickness, need generally a few thousand angstroms, to form good bulk films. Moreover, they are mostly transparent because they are wide-bandgap semiconductors. With proper choice of oxide semiconductor and by controlling the thickness of the interfacial layer, it should be possible to get solar cell performance equivalent to the p-n homojunction solar cells.

A simple equilibrium energy band diagram is shown in figure 3.8. As the operation of an SIS device is similar with that of an MIS, then the oxide-semiconductor to insulator barrier height $\phi_{osi}$ is the key parameter of this diagram and is known to control the degree of inversion of the p-type base semiconductor \textsuperscript{[30]. To invert
Figure 3.8

Energy band diagram of the SIS structure with the composition of ITO/SiO$_2$/p type silicon. (a) in thermal equilibrium, (b) under illumination.
the surface of the base semiconductor, it requires a low value of $\phi_{oii}$. As an example, if one side of the junction is p-type silicon, the insulator-semiconductor barrier height, which is taken from work-function data, is $\phi_{si} = 3.2$ eV. Suppose ITO material is placed on the other side of the junction, and it also has a low work-function which yields a $\phi_{oii} = 3.3$ eV, by virtue of the silicon and ITO work-functions, the surface of the p-type silicon is inverted. This low work-function material such as ITO on the surface of the device will invert the p-silicon surface, creating an electrostatic p-n junction on the surface of the silicon. The value of $\phi_{oii}$ is maximized at about 3.6 eV. Any value of $\phi_{oii} < 3.6$ eV is sufficient to do the inversion.

The inverted p-silicon provides a supply of minority carriers (electrons) which tunnel into the ITO. The wide bandgap of ITO, as already noted ($\approx 3.6$ eV), blocks the majority carriers which might be considered to be band-to-band tunnelling, so that this structure is forced to be a minority-carrier nonequilibrium SIS tunnel diode. The degree of tunnelling is a function of insulator thickness, (d). If the insulator thickness is too thick, the tunnelling mechanism would not function, and the device operates as a capacitor. The appreciable tunnel currents can flow when the insulator thickness is below 60 Å$^{[20,21,29]}$. If the insulator thickness is further reduced, the tunnel currents increase to the point where they are of significant magnitude so as to cause the semiconductors to depart from thermal equilibrium. This occurs around 20–30 Å for the ITO-Si system$^{[21,29]}$. Thus below some critical values of insulator
thickness "nonequilibrium" tunnel diodes are formed. This phenomenon is in agreement with the fundamental equations of any semiconductor devices which are nonlinear\textsuperscript{[80]}. For the insulator thickness less than 10 Å, it might become noncontinuous and the device more appropriately behaves like a Schottky barrier or p-n heterojunction rather than SIS diode. Therefore, in order to operate an SIS diode, the range of insulator thickness between 10 - 30 Å is the most suitable.

In the minority-carrier nonequilibrium mode of operation, the minority-carrier quasi-Fermi levels in the semiconductor could be pinned effectively to their respective minority-carrier bands over a limited bias range (see fig.3.8b) where the SIS diode has a forward bias $V_a$. As the junction is further forward biased, the semiconductor current increases eventually to a value larger than that which can be supported by the tunnelling process. This becomes the tunnel-limited regime of operation. At the start of this regime, the electron quasi-Fermi level becomes unpinned with respect to the conduction band edge. Prior this bias point, the SIS diode operates as a pseudo p-n junction and, in absence of defects, would be an ideal Shockley diode.

As proposed by Schewchun et. al the mechanism for current conduction in the device is created by tunneling through the insulator layer. The possible current flow in the device is shown in figure 3.8b. The minority carriers, which are provided by the inverted p-type silicon, are tunnelled into the ITO which is
denoted by $J_{CT}$. While majority carriers are blocked from tunneling by the wide ITO bandgap. Tunneling can also occur via defect states at the two interfaces. $J_{ST}$ is regarded to be the dominant tunnel transition via defects in ITO-Si system. $J_{CI}$ and $J_{VI}$ are the effective coupling current flows due to the interchange of charge between the conduction and valence bands of the silicon by recombination-generation. These two components contribute to the tunneling defects of $J_{ST}$.

3.3. SOME REPORTED PERFORMANCES OF SEMICONDUCTOR-BASED SOLAR CELLS USING CONDUCTIVE METAL-OXIDE WINDOW LAYERS.

Metal-oxide semiconductors of SnO$_2$, In$_2$O$_3$ and the mixture of indium and tin oxide (ITO) have been used for producing efficient solar cells as the n-type semiconductor window layers. The oxide-semiconductors (OS) belong to an interesting class of materials that behave as transparent semiconductors. Although they have large bandgaps (≈ 3 eV) they can be made degenerate, reaching values of resistivity as low as $2 \times 10^{-4}$ Ω cm that correspond to electron densities of $10^{21}$ cm$^{-3}$. Efficiencies ranging from 1% to over 12% were reported for OS/p-Si devices in the period 1975-1977$^{[25-27,31,32]}$ and equally good cells can be made on both p-Si$^{[28]}$ and n-Si$^{[27]}$.

The insertion of the insulating layer of about 10-30 Å thick has been found to have an advantageous effect mainly by increasing the $V_{oc}^{[32]}$ without decreasing $J_{sc}$ or FF. In properly controlled
insulating layers increases of up to 50% in $V_{oc}$ have been observed\cite{34}, since a portion of $V_{oc}$ is sustained across the insulator. This mechanism, according to Fonash\cite{33}, is called "field shaping". The insulator layer of above 35 Å will reduce the $J_{sc}$ and FF dramatically.

A variety of techniques exist for depositing oxide semiconductor (OS) onto silicon substrates, as has been mentioned previously. Ghosh et.al\cite{35,36} used an MIS model in their consideration of an $SnO_2/n$-Si cell. This was continued by Feng et.al\cite{37} by spraying $SnCl_4$ mixture onto heated n-silicon substrates to form an $SnO_2$ layer on the substrate. They obtained efficiencies, $\eta$, of 12.3% on single crystal and 10.1% on polycrystal silicon. These authors estimated a maximum theoretical efficiency of 20%. They concluded that the limit of the insulating thickness is such that the tunneling transition coefficient is unity and the role of the insulator reduces the effect of a bucking current due to thermionic emission.

Shewchun et.al\cite{14,20,21,38} reported that ITO/insulator/p-Si cells having efficiencies of $\eta = 12.8\%$. They proposed that current conduction is dominated by tunneling if the insulator layer is made at a proper thickness. They also presented efficiency as a function of insulator thickness, substrate carrier concentrations, surface state and oxide charge. The ITO composition of 9 mole% of $SnO_2$, which is deposited by sputtering, gave the best devices with $V_{oc} = 0.52$ V, $J_{sc} = 32$ mA/cm$^2$ and FF = 0.71 under AM1.2 sunlight.
These data are consistent with their theoretical prediction. The electron affinity and the interface state density are some of the critical features determining SIS diode operation. The electron affinity is controlled by the choice of the top semiconductor. The interface state density is controlled through the fabrication procedure, similar to controlling the thickness of the oxide interfacial layer. The cells they have had were claimed to be stable for 18 months when stored in laboratory conditions and measured periodically.

Thick-film screen printing techniques have recently been used for fabricating ITO/Si solar cells\textsuperscript{[59]} . They used a ready-made ITO paste and printed it onto the silicon substrates. Photovoltaic actions were found in these devices by showing a typical best cell of the junction behaviour in the dark-forward characteristics. The typical $V_{oc}$ was recorded between 280 - 293 mV with the FF of about 0.49. The most promising discovery they claimed is that the process was repeatable and by further improving of the ITO paste and the use of proper conditions of the growth of the oxide layer, it may give better cells. Similar experiments done by Saim et.al\textsuperscript{[40,41]} suffered from uncontrolled silicon oxide growth between the ITO and silicon substrate. They found that the thickness of oxide layers was about 60 to 100 Å. It was thought that a complex reaction occurred between the ITO layer and the silicon surface during fabrication, forming a much thicker interfacial oxide layer.
A decrease in the output of SnO$_2$/n-Si and ITO/p-Si with time has been reported to occur both at room temperature, and at an accelerated temperature rate at higher temperature$^{[42-44]}$. This degradation was presumed due to the growth in width of the insulator with time. Its implication for the practical use of the device involving MO or OS/Si junction, according to Maruska et al$^{[46]}$ has yet to be determined. They have shown the existence of two separate degradation mechanisms: one requiring optical excitation that increases $J_0$; and the other, a thermal mechanism that decreases the diode factor, $n$, and $J_L$.

3.4. THE ROLE OF THIN FILMS IN SOLAR CELLS.

Generally, there are three types of photovoltaic converter for terrestrial use. These are single crystal, concentrating systems, and thin film devices. Although the basic physics of the thin film devices is the most complex, they offer two important advantages:

1. Because the required thickness of the active layers is of the order of two or three times the optical absorption length, the material costs remain a small part of the total cost.
2. The thin film configuration lends itself to large area, continuous flow processing.

Direct conversion of solar energy to electric power by thin film photovoltaic devices appear to be the ideal solution. The major points on thin film photovoltaic can be summarized as follows
1. Efficiencies greater or equal to 10% on large areas appear to be feasible. Higher efficiencies and better stabilities are expected.

2. Cell performance is structure and deposition parameter sensitive, therefore better understanding of the structure sensitive properties, particularly at the interface, is necessary.

3. Some structures to form the device have been reported and demonstrated.

4. Research and development is required on crucial cases such as interface physics, composite thin film structures, gradient bandgap materials and properties, degradation processes and life time tests.

5. Material economy, energy economy and simple production processes make thin film solar cells a viable system.

Thin films are necessary not only for the photoelectrically active layers, but also for contacts, window materials, anti-reflection coatings and passivating layers. Equally important are the unique properties of thin films and the very large variety of deposition technique available to form the film. Methods of film deposition, therefore, play a role in developing useful solar cells. Some of the standard methods are vacuum evaporation (VE), non-reactive and reactive sputtering, molecular beam evaporation (MBE), epitaxial layer growth from liquid or vapour (LPE & VPE), chemical vapour deposition (CVD) and some other methods which need
to be considered. The spray pyrolysis process and the chemical deposition techniques are particularly attractive for large-area devices. These two processes have been developed to coat substrates of dimension of the order of 1m x 1m, reproducibly and uniformly\textsuperscript{[45]}. 

To illustrate the variety of possible types of materials systems that might contribute meaningfully to photovoltaic solar cells, a summary of experimental systems is given in Table III.1. In almost cases, the physics of thin films are polycrystalline. The individual crystallites are generally of good quality, but these are interrupted by numerous grain boundaries and perhaps occasional voids. These make the thin films appear somewhat complicated, therefore, in order to obtain a good quality of the film, some constraints have to be followed.
Table 3.1
Illustrative thin film photovoltaic systems and parameters

<table>
<thead>
<tr>
<th>Description of cell</th>
<th>$V_{oc}$ (Volt)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>Eff, $\eta$ (%)</th>
<th>Year</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO deposited by magneto-sputtering on InP single crystal to produce ITO/InP solar cell</td>
<td>0.5-0.6</td>
<td>17-18.9</td>
<td>9.6-12 (AM1)</td>
<td>1988</td>
<td>46</td>
</tr>
<tr>
<td>n⁺/p-InP solar cells deposited by metalo-organic CVD on Silicon substrate.</td>
<td>0.6-0.7</td>
<td>25-27</td>
<td>7.1-9.4 (AM0)</td>
<td>1989</td>
<td>47</td>
</tr>
<tr>
<td>InP Solar cell made by ion implantation</td>
<td>0.83-0.87</td>
<td>33-35</td>
<td>17-18.8 (AM0)</td>
<td>1988</td>
<td>48</td>
</tr>
<tr>
<td>Indium-tin-oxide (ITO)/silicon junction</td>
<td>0.51</td>
<td>32</td>
<td>12 (AM 1.5)</td>
<td>1976</td>
<td>26</td>
</tr>
<tr>
<td>CdZnS/CuInSe₂ heterojunction</td>
<td>0.43</td>
<td>37</td>
<td>11.3 (AM 1.5)</td>
<td>1989</td>
<td>49</td>
</tr>
<tr>
<td>CdS/CuInSe₂ made by CVD</td>
<td>0.42</td>
<td>34</td>
<td>10.8 (AM 1.5)</td>
<td>1986</td>
<td>50</td>
</tr>
<tr>
<td>GaAs p-n junction on Ge (tandem solar cell) fabricated by OMVPE</td>
<td>1.23</td>
<td>31</td>
<td>22 (AM 1.5)</td>
<td>1989</td>
<td>51</td>
</tr>
<tr>
<td>AlGaAs/GaAs tandem solar cell made by molecular beam epitaxy (MBE)</td>
<td>2.1</td>
<td>13.8</td>
<td>20.2 (AM 1.5)</td>
<td>1989</td>
<td>52</td>
</tr>
<tr>
<td>n⁺-pp⁺ structure InP solar cell grown by OMVPE</td>
<td>0.83</td>
<td>30</td>
<td>20 (AM 1.5)</td>
<td>1987</td>
<td>53</td>
</tr>
</tbody>
</table>
3.5. SUMMARY.

An overview of some solar cell structures has been given. The main mechanism of converting the light energy into electrical energy is receiving the photon from the light on the surface of a simple diode, then the photovoltaic effect will occur in the device. Two types of light absorption occur. These are useful absorption which will result in the generation of electron-hole pairs, which eventually produce a current transport, and parasitic absorption, mostly resulting in heat. The voltage, which is developed by the device, is a result of the difference between equilibrium built in voltage and the built in voltage due to the bias from the photon light. The parasitic absorption could be reflection or transmission of the light. The useful absorption should possess an energy photon equal or slightly higher than the bandgap of the semiconductor ($E_{ph} \geq E_g$). The solar cell model is explained in the simple manner using a homojunction p/n device, as it is a well established structure.

There are some structures, apart from homojunction, which are commonly employed for constructing the solar cell. These are heterojunction, Schottky barrier and heterostructure of MIS/SIS junction. A heterojunction is defined as a junction made of two different semiconductors on either side of the junction, and thus also has difference in bandgaps, electron affinities and work-functions. The different properties of the materials make the junction seem complicated. However, by a proper choice of the property of the materials, a good device is very likely to be produced.
A Schottky barrier, which is a metal-semiconductor junction, is attractive due to simplicity of fabrication and the promise of a relatively inexpensive processing technology. The potential drop of this junction occurs in the semiconductor side of the junction which give rise to a depletion region at the interface as in the p/n junction case, which is known as Schottky diode. This depletion region has rectifying and photovoltaic properties. The metal in this junction acts as a heavily doped semiconductor.

Heterostructures of MIS/SIS junctions are very similar to the metal-semiconductor junction except that an insulator is inserted in between the two materials. The incorporation of a purposely grown insulating layer has an advantageous effect of the open circuit voltage compare to the M-S junction. The insulating layer is generally between 10 to 30 Å\[^{10}\]. If the thickness of the insulator layer is less than 10 Å, device will act as a Schottky diode. The insertion of insulating layer between semiconductor-semiconductor junction results in SIS structures. Some theoretical models have been explained.

Performances of semiconductor-based solar cells using conductive metal oxide as a window layer have been reviewed. Efficiency conversion more than 10 % have been achieved confidently. The use of thin film solar cells seems a very suitable solution for a large production, since the thickness requirement of active thin films is very small. Their configurations make possible to produce a large area by continuous flow processing.
REFERENCES.


CHAPTER IV.

THICK FILM TECHNOLOGY.

4.1. THE DEVELOPMENT OF THICK FILM TECHNOLOGY.

Thick film technology emerged in the early 1960s\cite{1,2}, when the electronic industry was in search of a new approach to miniaturisation which could lead to a low-cost, reliable and small electronic system of high complexity. Thin-film microcircuits were established at that time, as they were capable of providing resistor and capacitor film devices with considerable precision and stability. It was therefore projected that "integrated circuits" incorporating thin film resistors, capacitors, inductors and eventually active transistor devices would provide an answer to most circuit fabrication problems. The thick-film screen printing system was developed subsequently, and was claimed to be considerably simpler in processing and low-cost in production, where extremes of accuracy and stability were not critically required.

Since then, the thin-film and thick-film technologies have complemented each other in many applications as both are suitable for low volume circuits, complex arrays and applications requiring medium to high power, high voltage or stable components. In microwave applications, however, thin film hybrids are favourable because of the need for critical precision control and component
value. The advantages of using thick-film technology are its flexibility, good tolerances and low initial capital investment\cite{3}. These are the reasons for the success and rapid expansion of thick-film utilizations in industry. Moreover, circuit designs may be rapidly and economically implemented in production even for the small volumes, since the manufacturing process is relatively simple and "in-house" facilities are economically feasible for smaller companies. In general, thick film hybrid circuits can be produced more economically, with no compromise in performance, than can thin film ones.

The technology is now entering a phase in which it is progressively displacing the printed circuit board systems in many applications. It is also playing its part in the expanding field of microelectronics since it is already widespread. A growing area of use is also in the manufacture of precision instrument and control systems, where the extremes of ruggedness and stability are not required, but the low cost is important\cite{3}. The application in thick-film hybrid circuits is that the active devices are added as discrete elements, so that the problems of performance tolerance due to the sensitivity of performance characteristics of materials to processing conditions can be avoided, since chips or packaged devices have been preselected and tested to a required tolerance. Since this technology is capable of providing precision in passive components, by adding some discrete active devices, it is possible to utilise the thick-film approach to build circuits precisely tailored to a specific performance required.
In solar cell applications, thick-film technology is mostly used for metallisations and anti-reflection coatings to enhance the performance of the cells[5]. As reducing the production cost is an important factor, this technology can replace the conventional vacuum evaporation which suffers from a number of disadvantages such as low throughput, high capital investment, and low-deposition yields. In addition this technology can also be used to make a junction formation in the silicon solar cell[6-7] where it has an advantage that there is no parasitic junction formed on the back of the wafer as in the case of an open tube diffusion.

Thick film technology is commonly defined in the description for the field of microelectronics. In this technology specially formulated pastes are applied onto a substrate (e.g. alumina, glass or semiconductor wafer) in pre-defined patterns and sequences to produce a set of individual components such as conductors, resistors or capacitors. When dried and fired, these prints can produce the required properties. The typical thickness of fired films will be between 10 and 25 microns[1,4].

4.2. THE DEPOSITION PROCESS AND MATERIALS.

Screen printing is the basic operation in thick-film technology. It is a stencil process in which the printing medium, paste or ink, is forced through the openings of the mesh-reinforced stencil (the pattern), then the paste will be printed
out onto the surface of the workpiece or substrate. The mesh fabric of the screen performs the dual function of holding together the various parts of the screen and also, by virtue of its thickness, metering the thickness of the paste deposit.

There are two modes which are generally used. These are (a) "in contact" printing and (b) "out of contact" printing. The latter mode is more often used, and this has been used throughout this work. In "out of contact" printing, the screen is held parallel to and slightly above the surface of the substrate (Fig.4.1). The separation between the two, often referred to as the "snap off distance", varies according to the size and type of screen, paste rheology, and printing conditions being used.

The printing medium (ink or paste) is applied to the upper surface of the screen and a flexible squeegee is traversed across the pattern area. The passage of the squeegee presses the screen into contact with the substrate surface and forces the paste through the open meshes of the screen. Behind the squeegee the screen, by virtue of its tension, peels away from the substrate leaving a printed pattern of ink/paste on the substrate. Snap-off-distance is not used with "in contact" printing. The screen and the substrate remain "in contact" throughout the printing stroke and are separated mechanically after the completion of the squeegee traverse.

The inks or pastes are composed of a viscous mass containing
Figure 4.1
Basic diagram of "out of contact" printing.
(Ref 4)
four main elements. These are: (i) active powder, (ii) frit, (iii) organic binders and (iv) solvents.

(i) Active powder is the functional element in the paste. After firing, it will determine the properties of the layer. The powder is sintered during firing at temperatures varying from 550 to 900 °C. The mean grain size varies from less than one to three microns[^1] and should be kept as small as possible to obtain a low sintering temperature.

(ii) For frit, normally glass powder with a low melting point is used. This will ensure contact between the metal particles during sintering and causes the adhesion of the paste onto the substrate. The viscosity properties of the glass as a function of the temperature determine the temperature range in which the paste must be fired. Typical frits are oxides of boron, bismuth, lead or the mixture of these oxides.

(iii) Organic binders keep the active powder in suspension. They burn off during the firing process.

(iv) Solvents are necessary to adjust the viscosity of the paste during the printing process. They evaporate during drying at a temperature of 150 °C.

The viscosity requirements for a paste are complex. During the screen printing process the paste must be liquid enough to
flow through the screen, whereas immediately after printing, the viscosity must increase allowing levelling off of the surface. Some of the pastes are "thixotropic mixtures" - that is, the viscosity of the paste is reduced when pressure or energy from the squeegee is applied. This is the reason the ink "stands" on the screen, flows through as the squeegee applies pressure, and when the pressure is released, "stands" again as a line without any further flow. These special pastes are useful for fine-line printing applications.

Adjusting the viscosity of the paste is simply adding the solvent to a specified value. However, care must be taken in adding the solvent for adjusting the viscosity since the rheological properties of the paste are complicated. The pastes must show the proper amount of yield, so that, under the force used in screen printing, flow will occur and the material will then stiffen and remain in position. In addition, viscosity adjustment should not alter the main properties of the final product.

4.3. THE PRINTING MACHINE[^8].

A stencil screen, which defines the printed pattern, is one of the most important parts of the screen printing technique. It serves both to delineate the pattern to be printed, and to act as a metering device for the deposition of a precise quantity of the ink/paste. Another important part is a squeegee, with which the
printing medium (ink/paste) is forced through the screen onto the surface of the substrate. In order to obtain the accurate location of the printed pattern it is necessary to provide a means of registering the screen with respect to the substrate and this is the primary function of the printing machine. A wide range of printing machines is available, from the simplest hand operated machine up to fully automated production equipment capable of printing thousands of substrates per hour.

The three basic features of the common printing machine are
(a) the screen mounting
(b) the substrate holder
(c) The squeegee and its control mechanism.

Some printing machines, mostly the completely automatic types, incorporate other features which may be associated with either the screen mounting or the substrate holder such as a means of moving the substrate or the screen from the substrate loading to the printing position, or a mechanism for precise adjustment of the relative position of the screen and the substrate.

4.3.1. The Screen.

The screen consists of a screen mesh which is mounted on the screen frame. The screen mesh serves as a support for the stencil and it is formed by a mesh, either stainless steel wire, polyester, or plastic nylon, where each has advantages for
particular applications. The different screens are characterized by their area, the number of wires per inch (called the meshnumber) and the orientation of wires/threads with respect to the frame. The number of wires/threads per inch determines the fineness of the meshes. The woven-mesh is pre-tensioned prior to attaching to the screen frames by clamping the square or rectangular piece of mesh and stretching it in each direction to maintain uniform shape and tension.

Comparison of the three mesh materials has been made by Franconville et.al[9], and shows that the stainless steel wire is the most reliable. It is generally selected as the most desirable mesh material for precise fine-line printing. It is also much harder and more abrasion resistant and also normally lasts and wears longer than nylon or polyester materials. The greater flexibility of polyester or nylon mesh may be used to advantage when printing over very irregular surfaces[13], whereas stainless steel mesh could easily be damaged for this particular application.

The thickness of the mesh and its percentage of open area are the primary factors controlling the amount of ink deposited during printing although in some cases this may be modified by building up the stencil-forming material on the working face of the screen. The percentage of open area at any given mesh count is dependent on the wire diameter and it is sometimes possible to obtain several wire diameters at the same mesh count (meshnumber).
There are three types of emulsion for defining the mask on the mesh screen, namely direct, indirect, and combination direct and indirect\(^9\). All these types rely on a process of photopolymerization of an ultra-violet sensitive emulsion. The direct and combination direct-indirect methods give long life and good definition, but have the disadvantage that their preparation is long and complex. These methods are mostly used for high accuracy applications, and suitable for mask production, while indirect screens, on the other hand, are usually used in low yields application and do not have the length of life obtainable by the other methods. An advantage of the indirect method is that it gives greater uniformity of emulsion thickness and superior line definition. This type of screen was used throughout this work.

Screen frames, which are used for supporting the woven mesh, are produced from plastics including phenolics\(^9\), or metal. Most screen frames are made of cast aluminium. This is because of the light weight, strength, stability and reusability. However, the aluminium frames are often warped as a result of the casting process\(^9\). This can be eliminated by machining the frame to a specific thickness with the bottom surface flat and parallel to the top surface. Machining also eliminates uneven stress points such as burrs and projections on the mounting surfaces for the screen mesh.
Another critical feature in the screen is attaching woven mesh to the screen frame. There are several methods of attaching the mesh onto the frame. The most reliable method is epoxy-adhesive mounting. This method allows the mesh to be mounted on the frame with very high tension without any danger of the mesh shifting on the frame which could occur in other methods such as mechanical clamping or crimping.

4.3.2. The Screen mounting.

The screen mounting must provide a means of holding and accurately positioning the screen, both horizontally and vertically, and must be sufficiently rigid to resist the forces imposed on it during the operation of the printer. In "out of contact" printing, the vertical separation of the screen from the substrate is often critical and this may have to be set so that the parallelism between the substrate and the screen meets the requirements of the printed pattern. In some circuits, the printed pattern is required to be accurate between 25 and 50 μm. These figures are the total tolerance in providing the pattern on the substrate and include inaccuracy due to screen mounting, substrate holder positioning and registration of substrate in the substrate holder.

While the screen mounting must hold the screen rigidly during printing, it normally permits rapid removal and replacement of screens without losing their accuracy. For this reason, some
machines have a separate screen carrier or chase in which the screen is mounted, and which may be located accurately in the machine. The screen chases are important for adjusting the pattern on the screen which is going to be printed onto the desired area on the substrate. This is carried out by adjusting the screen in the X, Y and rotational sense to allow adjustment of the screen relative to the substrate, also vertical adjustment in order to establish the parallel gap between the screen and the substrate may be made. Common parallel gaps are between 0.01 in and 0.04 in$^{[3,10]}$ for a screen with a size of approximately 5 x 5 in. These gaps are important since they are one factor which controls the amount of paste delivered to the substrate and the precision of the printed pattern.

Other important considerations of the screen mounting are that it should allow access to the screen face for cleaning without loss of its registration, and it should leave the screen unobstructed during preliminary setting up and alignment of the pattern with the substrate.

4.3.3. The Substrate Holder.

The substrate holder is required to register the substrate accurately below the screen and hold it rigidly in position during the deposition of the print. This holder comprises a platform having a recess in which the substrate is positioned. The substrate is normally located by butting two adjacent edges firmly
against datum surfaces in the recess. A vacuum is applied through the holes in its base to aid retention of the substrate in the recess.

The substrate holder is mounted on a moving carriage which travel from a loading position remote from the screen to the print position beneath the screen. The carriage movement must be both accurate and a precise mechanism to ensure that the substrate to screen registration in the print position is accurately repeated. In some machines, however, the substrate holder remains stationary and the screen is mounted on an upper platen which moves vertically on precision ground die posts. The substrate is loaded into the holder and the upper platen is moved vertically down on the die posts in a similar manner to that of a precision metal stamping die press.

4.3.4. The Squeegee and Its Mechanism.

The squeegee or a flexible blade is drawn across the back face of the screen during printing with an inclined edge. It is generally made from natural or synthetic rubbers with a certain hardness required for particular paste and circuit. The material used must be resistant to the organic solvents used in thick film pastes and must provide a flexible edge in order to follow any unevenness in the substrate surface. However, it should also have sufficient rigidity to maintain a fixed angle of attack and be hard enough to ensure accurate cut-off of the paste or ink. The
squeegee blade stocks are normally extruded strips of square or rectangular cross-section and are mounted in the machine to give an attack angle of about $45^\circ$. Figure (4.2) shows the most commonly used squeegee blade configurations.

During the printing process, the squeegee moves across the back of the screen, pressing it into close contact with the substrate and sweeping a quantity of printing medium over the pattern area. The angle of the squeegee and its traverse speed generate a pressure within the viscous paste which forces it through the open meshes of the screen and onto the substrate surface. As the squeegee passes each mesh opening it cuts-off the paste to the level of the screen fabrics, thus metering the quantity of material which can be transferred to the substrate. The composition, shape, and motion of the squeegee are of great importance in screen printing as they, in combination with the screen, are the main variables controlling the definition and thickness of the print.

Squeegee traverse speed has a significant effect on the fluid pressure generated in the paste. The higher speeds produce greater pressure, but simultaneously reduce the time available for the paste to flow through the mesh openings and, in "out of contact" printing, increase the speed of separation of the screen from the substrate. The behaviour of the paste under these changing conditions is further complicated by its rheological nature\textsuperscript{[12]}. This makes it very difficult to predict the reliability from paste
Figure 4.2.

Some common squeegee blade configurations.

(Ref 4.)
to paste under the effect of such speed. It is often the case, however, that deposit thickness is mostly constant at lower squeegee velocities\(^{[14]}\), increasing slightly to a maximum at intermediate speeds and then falling sharply at high stroke speeds due to incomplete filling or poor transfer of paste from the screen at high screen/substrate separation rates.

The squeegee holder may be mounted rigidly or may be of the floating, or swivelling, type which is pivoted to enable it to align itself parallel to the screen and substrate. The majority of machines use a rigid squeegee mount although many of these are provided with adjustments for squeegee realignment which is necessary if the rubber blade needs to be cleaned or changed. A few are also fitted with a means of adjusting the angle of attack. Some other machines are fitted with demountable squeegee holders which can be easily removed and replaced accurately in the machine, thus facilitating thorough cleaning and inspection of the blade edge.

In some machines, the printing stroke is unidirectional. The squeegee remains in contact with the screen only on the forward stroke, then is raised out of contact on the reverse stroke. In this case, a flood blade is provided to return the excess paste to the starting point during the reverse stroke prior the next printing cycle. In other machines, provision is made for two directional printing, the squeegee remaining in contact with the screen on both advance and return movements.
Squeegee down pressure may be applied by several methods. The most commonly used are spring, torsion bar, pneumatic and dead weight load. It is essential to ensure smooth movement of the squeegee over the screen avoiding erratic travel which is characterized by a juddering motion of the squeegee assembly. For this reason a damped hydraulic system, rather than a pneumatic drive system, is often used.

In applications where accurate control of deposit thickness is important, the squeegee and flood blade arrangement must ensure that the paste does not accumulate on the back face of the squeegee as the paste reaching this position may subsequently be smeared across the screen behind the squeegee blade. Smearing of this kind prevents accurate metering of the paste and causes localized variations in print thickness. This effect is often observed when printing a large area.

4.4. DRYING AND FIRING.

Printed thick film circuits are subjected to a drying and firing cycle during which the organic vehicle is removed, and a series of chemical and physical reactions occur which develop the electrical properties of various pastes. The drying stage is intended to remove the volatile organic solvents and make the print, which still contains organic binders, adherent to the substrate and immune to smudging. After this stage, the substrate
may progress to high temperature firing or may be over-printed with additional circuit elements.

Drying is a relatively low temperature process. The common drying temperature is between 70 and 150 °C for a period ranging from 10 to 30 minutes depending upon the composition as well as on the method adopted. It is normally insensitive to the operating conditions providing that heating rates are not so high as to cause violent evaporation of the solvent and consequent disruption of the print surface. Infra-red or warm air heating is generally used for print drying and both of them have been claimed to have satisfactory results.

In laboratory or small scale production, wet prints may be batch dried in ovens, but it should be noted that many solvents used in thick-film pastes are inflammable and precautions must be taken to avoid dangerous accumulation of vapour. In commercial manufacture, drying is normally carried out in a moving belt drier heated either by infra-red sources arranged above and below the belt or by warm air circulation. Belt driers of this type are often used as conveyor belts to link the printer with the next production stage which may be inspection, high temperature firing or a further printing stage.

The firing process is a continuation of a drying stage. This process is intended to develop the ultimate properties of the prints. It involves a high temperature cycle and is designed to
remove any remaining organic binders left over from drying, to adhere the circuit elements to the substrate and eventually to develop the final properties. The range of firing temperature is generally between 450 and 1000 °C and usually involves three stages of processes. During the first stage, the remaining solvents are volatilised and the organic binder is carbonized and oxidised. These processes occur at fairly low temperatures between 200 and 350 °C and require an oxidising atmosphere. At the second stage, in which the printed circuits are taken to the maximum firing temperature (up to 1000 °C), the glass component of the paste melts to form a vitreous medium which serves to consolidate the printed layer, and also promotes adhesion to the ceramic substrate. In this way the final characteristics of the pastes are developed. The final stage is cooling the completed circuit print. At this stage, the molten glass solidifies to form a coherent film. Some of the pastes are sensitive to the cooling process and need gentle cooling, whereas a few of them need rapid cooling to quench the printed film. Conductor pastes are mostly insensitive at this stage.

As the developing of the printing circuits follows several stages, thick-film circuits are, in nearly all cases, fired in a multi-zone, continuous/moving belt furnace in which the speed of the belt and the temperature in each zone are controlled to correspond to the time-temperature curve appropriate to the material being fired. Each furnace zone is normally heated independently and is independently sensed and controlled by means
of a separate thermocouple and control system. This is aimed to enable the required temperature profile to be established. Typical time-temperature firing curves are illustrated in Figure 4.3. Most furnaces have similar basic design (see Fig. 4.4) in which an endless metal chain mesh belt is drawn through a muffle tube. The width of the chain belt varies from 10 to 50 cm. The belt assembly is normally driven by a variable speed motor which provides controllable belt speeds from 1 to 15 cm per minute.

The tube is heated from the outside by resistance windings, generally of "Nichrome" or "Kanthal", which are arranged in a series of separate zones, each regulated by a proportional type temperature controller. The tube itself may be round, rectangular, or D-shaped in cross-section and is made from ceramic, fused quartz or metal muffles. Fused quartz muffles are often used in furnaces since this material is inert in an oxidising atmosphere up to 1000°C.

Control of atmosphere and its rate of flow through the furnace are important. A simple method of maintaining a reasonable degree of control in the flow rate is to incline the furnace at an angle of between 1 and 3 degrees, to induce a flow of air through the furnace towards the loading end (see Fig. 4.4). This is done so that the printed circuits being fired in the hottest zone always encounter an uncontaminated supply of air, since all combustion products will be swept out of the furnace over the oncoming circuits at a relatively low temperature. Some furnaces have facilities for maintaining different atmospheres in the preheat
Figure 4.3

Typical time—temperature firing profile.

(Ref 3)
Figure 4.4
Basic design of a thick film moving belt furnace.
(Ref 4.)
zone in which oxidation of the organic materials occurs, and in the sintering zone in which the final firing of the composition occurs.

4.5. SUMMARY.

An introduction to thick-film technology has been given. The early demand of this technology was to produce low cost and reliable electronic components where extremes of accuracy and stability were not required. The advantages of this technology are its flexibility, reasonable good tolerances and low initial capital investment. Therefore it is possible to be run by smaller companies since the small volumes of production are still economically feasible.

The basic operation of this technology is a screen printing process. It is a stencil screen process in which the printing medium, paste or ink, is forced through the opening of the mesh-reinforced stencil, then the paste will be printed out onto the workpiece or substrate. "In contact" and "out of contact" printing are generally used for depositing the paste. The composition of the paste consists of active powder, frit, organic binders and solvent.

There are three main apparatuses involved in this technology. These are the screen, the printing machine and the furnace. The screen consists of a screen mesh which is mounted on the screen frame and the screen mesh serves as a support for the stencil. The stencil screen defines the printed pattern on the substrate.
It serves both to delineate the pattern to be printed and to act as a metering device for the deposition of a precise quantity of the paste. The printing machine provides a means of registering the screen with respect to the substrate. There are three basic features of the common printing machine; these are the screen mounting, the substrate holder and the squeegee.

As the thick film circuits are subjected to drying and firing, the furnace then plays the major role in this technology. During firing, the organic vehicle is removed and a series of chemical and physical reactions occur which develop the eventual properties of the paste. Some mechanisms of the furnace for developing the films are discussed.
REFERENCES.


5.1. PREPARATION OF ITO FILMS USING SCREEN PRINTING.

There are three main apparatuses involved in the development of the ITO films. These are the screen, the printing machine and the furnace (see Figure 5.1). These three apparatuses are commercially available and explanation of these has been given in the previous chapter. Preparing the screen with the required pattern is the starting point in the design of any thick-film circuit. The lay out of the art-work of the required pattern is drawn on graph paper at a magnified scale, usually ten to one. The material for making the art-work is a translucent sheet, "cut and peel"; a red film attached on the surface of a clear mylar. By tracing the pattern on the graph paper, the final art-work is delineated by peeling off the red film on the "cut and peel" using a scalpel. The pattern of the red film is then removed, leaving the area where the film is to be printed.

The final art-work needs to be photoreduced in order to meet the required size of the substrates. The original art-work is attached to the camera copy-board which is back-lit for best contrast. By using a camera, the pattern is automatically photoreduced onto a negative film. The required size of the photoreduction is obtained by adjusting
Figure 5.1 (a) : A photograph of screens used in the screen printing process with 3 different pattern.

Figure 5.1 (b) : Moving belt furnace of BTU SYSTEMS.
Figure 5.1 (c) : A DEK 1200 semiautomatic printer.
the distance between the camera and the copy-board. After subsequent developing and drying, the film is ready for use for making the required pattern on the screen. The sequence of pattern-making is illustrated in figure 5.2.

5.1.1. Screen Making.

The emulsion thickness used for pattern-making on the screen was made up in one process by applying a ready made direct emulsion-film attached to a plastic carrier. The capillary method of direct emulsion-film[1] was used in the process as this was most convenient. It gives good control over the emulsion thickness. The first stage of the screen preparation was cleaning using trichloroethylene followed by acetone. Stainless steel screens with 200, 325 and 400 mesh were used in this work. A piece of emulsion-film about 4 x 3 inches was placed in the centre of the damp screen. The moistured softens the film emulsion which was then attracted, by capillary action, up into the mesh structure. A single squeegee stroke skimmed off excess water, and speeded the drying. After it was completely dried, the plastic carrier for the emulsion was then peeled off in one smooth stroke, and the screen was ready for exposure under UV light to develop the pattern.

The screen, with the emulsion on top of it, was placed on the exposure unit contact frame with the emulsion side up. After the negative film was placed on top of the emulsion sheet, the screen
Figure 5.2.
A sequence of pattern-making process on the screen.
was then exposed to the ultra-violet light. The exposure time for photopolymerization of the emulsion was about 6 to 8 minutes depending how fine the pattern was. The development of the pattern image on the screen is carried out by using luke warm water poured on the pattern. The unexposed portions were removed in the development process. Those parts that were exposed to the ultra-violet light were unaffected by the water. The screen was then inspected under a microscope for blockages, pinholes and bad definition. After inspection for the quality of the pattern, screen filler was applied to cover areas surrounding the pattern which were still open. The final stage was drying the screen thoroughly which was then stored in a dust free place until it was ready for printing.

5.1.2. Printing The Film.

The printing process depends essentially on the forcing of an ink or paste through a stencil pattern comprised of a fine mesh. A semi-automatic "DEK 1200" screen printer was used throughout this work for printing ITO paste and metal pastes for contact purposes. ITO paste number 3050 made from Electro Science Laboratory (ESL) was mostly used and occasionally, ITO paste number T.1010 from Electronic Research Administration (ERA) was also used in the preliminary investigation. The T.1010-ITO paste from ERA was abandoned for further application in this work, since it gave the same results as the ITO type 3050 from ESL. Moreover, the handling processes of the ERA paste were slightly different
from those of ESL paste. Sometimes the ITO films from the ERA paste did not develop satisfactorily.

Stainless steel screens of 325 and 400 mesh were used for printing the ITO films because they gave good control of the film thickness. Squeegee pressure, during printing, was kept at a constant setting of 6 on the DEK printer, because this pressure was also contributing to the control of the quantity of the paste which transferred to the substrate. 1 x 2 inch of alumina substrates were mostly used in the preliminary work for supporting the ITO films. For optical measurements borosilicate glass was used. The substrates were cleaned, before use, in an ultrasonic cleaner for 30 - 60 minutes using trichloroethylene followed with acetone. The geometry of the printed ITO films was (1x1) cm. This was chosen in order to simplify the calculations.

A ready patterned screen was then loaded on to the printer and the substrate was loaded on the substrate holder and was then rigidly held by a vacuum. The distance between the substrate and the screen (snap off distance) was adjusted in such a way as to give an average film thickness of about 200 - 250 nm. This is important since it is one factor which controls both the amount of paste delivered through the screen and the precision of the printed pattern on the substrate. A small quantity of paste was dispensed on to the upper surface of the screen. A test sweep of the squeegee was necessary before the actual printing in order to level the paste on the screen. After the paste was properly
leveled, the printing of the films was carried out, depositing the printed paste pattern on the substrate.

Immediately after printing a pattern through a mesh type screen, the print was made up of a series of discrete paste spots, each corresponding to a mesh opening. The fresh printed film must therefore be allowed to stand at ambient temperature. This was to make the ink coalesce in order to form a coherent, level film in which the mesh pattern was no longer visible. For the ITO paste used in this work, 10–15 minutes was found to be adequate. After the coalescence time, the prints were dried in an oven to remove the more volatile ink components. The temperature used for drying was 130 °C for 15 minutes, which was the time-temperature standard recommended by the manufacturer for typical ITO paste used in this work. At this stage, the prints started to adhere to the substrate and the smudging from foreign objects could be minimized.

5.1.3. Firing The Film.

Firing is the most important process since the ultimate properties of the printed films are developed in this stage. During printing, the remaining solvents were volatilized and organic binders carbonised and oxidised. As mentioned in the previous chapter, the firing process involved three stages which took place continuously in the same furnace. The temperature profile for each stage is illustrated in figure 5.3.
Figure 5.3

Firing profile for the ITO paste.
A choice of two furnaces for firing was available. A "DEK 840" is a laboratory type furnace which has only a single heated zone. It gave good control over the firing profile with facilities to provide rapid cooling which is necessary for quenching\textsuperscript{2}, but, it lacked provision for circulating compressed air over the substrate to blow away the volatile components and combustion products. The belt can be programmed to run continuously or to stop for a preset dwell time at the centre of the heat zone. This dwell time can be varied to give differing periods at peak temperature. A timer with a synchronous motor can be set to provide a variable dwell time up to 15 minutes. If the time required is more than 15 minutes, the dwell time should be reset, immediately at the end of the first period, for the amount of the additional time required. After the dwell time has elapsed, the belt is automatically started again and runs until the cycle is completed.

A "BTU SYSTEM" furnace of the "QA SERIES" is bigger than the DEK furnace. It is designed for production line processing of thick film as well as for laboratory research and development\textsuperscript{3}. It provides a facility of allowing a compressed atmosphere to blow away unnecessary products in the first stage of firing. It is provided with atmosphere flow controls which have independant inlets for preheat and firing sections. Supplies of other inert gases and other non-explosive atmospheres can be used since five flowmeters are provided for various atmospheres, such as dry air or mixture of nitrogen and oxygen. The atmosphere control system ensures a uniform flow of a controlled conditioned atmosphere in
the burnout and firing sections. In the burnout section, removal of product contaminants and the reduction muffle back pressure is controlled by the ejection of air from the entrance exhaust venturi located within the entrance flue. Burnout atmosphere (large volume - high velocity) is supplied in a manner which ensures even distribution and uniform flow over the product. In the firing section, gas removal and back pressure are controlled by the exhaust venturi located within the exhaust stack. The firing section atmosphere is preheated and diffused to create a controlled, uniform flow.

This type of furnace is equipped with 4 controlled heat zones, each of which are controlled by a solid state proportional controller, range 200 - 1200 °C with an accuracy of ≈ 0.5 °C. The temperature within the furnace is sensed by a thermocouple and the signal from the thermocouple is amplified by the controller and fed to a higher level control system.

The main muffle section through the heating chamber is made of fused quartz. This is a non-contaminating quartz muffle and is designed to allow the metal conveyor belt to ride directly on the quartz hearth, eliminating the need for a metallic hearth. The friction of a metal belt on a quartz surface is less than 50% the friction of a metal hearth, thus, prolonging the life of the belt. The belt used is 10 cm wide NiCr mesh with. It is driven by a d.c motor working in a closed loop system. The belt speed can be adjusted over the range of 1.27 - 7.6 cm/min. Layout of this
furnace is drawn in figure 5.4.

Both of these furnaces were used in this work. Each was used for specific purposes. For firing the ITO films, the BTU-SYSTEM furnace was mostly used since it is equipped with more accurate facilities such as an atmosphere control system and four different heating zones. The dried prints were placed onto the loading belt area which can be loaded with a number of substrates while the belt is running. The belt speed was adjusted at dial setting of 62.5, which is equivalent to an average belt speed of 1.4 cm/minute. This speed setting gave an average firing time of 30 minutes in the peak firing temperature area. The quality of fired films using this furnace was satisfactory in terms of physical observation, since the stress of the substrate had been controlled by preheating and cooling rates. Moreover, atmosphere control contributed to the quality of the results.

5.1.4. Annealing.

Annealing treatment is an important process for improving the quality of the electrical and optical properties of the films\textsuperscript{10-12}. Annealing treatments of the printed ITO films have been carried out in various ways such as annealing in air, under argon and in a vacuum. In annealing in the oven, with air or argon ambient, the rate of the heating process was monitored every 25 °C, and every 10 °C during cooling. During annealing in argon
Figure 5.4.

Lay out of BTU furnace of QA series.
ambient, samples were placed in a small metal box containing 5 samples. Two small holes at both ends of the box acted as an inlet and outlet for the argon gas supply.

An "Edward" vacuum system, model "E-12", was used for annealing the films. It was equipped with an inlet channel to the vacuum chamber for allowing gas supply if necessary. Annealing in a vacuum with and without argon gas injection was carried out at a maximum temperature of 300 °C.

5.2. ELECTRICAL CHARACTERIZATION.

5.2.1 Sheet Resistance Measurement.

Sheet resistance measurement is one of the basic semiconductor parameters with which the resistivity or conductivity of the film can be determined. There were three methods used in this experiment. These were two contact method, four contact method and four point probe. The last method was mostly used for measuring the sheet resistance while the other two were used as back up facilities in case the main method could not be used, i.e. measuring in the vacuum chamber.

The first method (fig 5.5a) suffered from the geometrical shape of the films. The value of the sheet resistance was always changing every time the geometry of the film was altered. This was
Figure 5.5.

Some methods for measuring the sheet resistance and resistivity. (a) Two contact method, (b) Four contact method, (c) Four point probes.
thought to be due to a slight variation in the film thickness. The formulation used for this method is\textsuperscript{[4]}:

\[
R = \frac{R_s \cdot L}{W} 
\]

(5-1)

where \( R \) is the resistance measured by the meter, \( L \) is the length, \( W \) is the width, and \( R_s \) is the sheet resistance. Therefore, the geometry of the film was synchronised with the other methods in order to get the same results. Geometry of 1 x 1 cm, for particular, ITO films was found synchron with the other method.

The second method was more consistent, but, the samples which were used for this measurement cannot be used or processed any further since metal contacts had been attached to the films. Therefore, this method was only used for preliminary characterization of the samples. From the geometrical shape of figure 5.5b, the outside contacts were used to pass the known current, \( I \), (supplied by the current source) while two inner ones were used to measure the ensuing voltage (\( V \)). The relationship of those parameters, including the geometrical parameters is\textsuperscript{[5]}:

\[
R_s = \frac{W \cdot V}{L \cdot I} 
\]

(5-2)

The third method was a more practical, simpler way of getting the same results using a commercially obtainable probe, called a
"four point probe". These four probes are arranged in a line with each head having a springy metal point. The probe spacing is \( \approx 1 \) mm as illustrated in figure 5.5c. When the probe was lowered onto the film surface, the two outside points were used for passing the constant current while the inner two were used for the voltage measurement. For a film with thickness, \((d)\), much bigger than the distance between the probe \((s)\), and for a measurement performed far enough from the edge of the films, the resistivity is given by\(^5-7\):

\[
\rho = 2\pi s \frac{V}{I} \quad (\Omega \text{ cm}) \text{ for } s \ll d \quad \ldots \ldots \quad (5-3)
\]

If the thickness \((d)\) of the measured film is much less than \((s)\), then:

\[
\rho = \frac{\pi V}{\ln 2 I} \quad d \quad (\Omega \text{ cm}) \text{ for } s \gg d \quad \ldots \ldots \quad (5-4)
\]

Equation (5-4) can be re-written as:

\[
\rho = 4.53 \frac{V}{I} \quad \ldots \ldots \quad (5-5)
\]

In order to get the layer sheet resistance \((R_s)\), measured in "ohm per square", it can be defined as the resistance of an arbitrary size square of that layer:
This method is very useful for measuring very thin semiconductor layers and works in non-destructive way. Therefore, this method was mostly used in the experiment, since it is very easy to use and can be used at any time.

5.2.2. Hall Effect Measurement.

Another important measurement for electrical characterization is Hall effect measurement. This measurement is often used as an experimental tool to measure the carrier type, concentration and Hall mobility of the materials. A specific geometry of samples was required for the purpose of the Hall effect measurement. Practical requirements dictate an aspect ratio between the breadth and length of the samples of 1 : 6. The geometry and dimension used are shown in figure 5.6.

The ITO films, which were used for this measurement, were deposited on borosilicate glasses which were previously cleaned in an ultrasonic bath for a few minutes. Silver contacts, using ESL-590.G, were used at four different points as shown in figure 5.6. The firing temperature of ITO films was at 650 °C, which is claimed to be the optimum firing temperature for the ITO paste[8,9]. After the silver paste was printed, the samples were cofired, to develop the metal contact, at 500 °C.
Figure 5.6

Geometry of the ITO film for the Hall effect measurement.
(drawing is not to scale)
5.3. OPTICAL CHARACTERIZATION.

Refractive index and transmissivity are important parameters of the ITO film being used. Refractive index of the films was measured using an ellipsometer, which also measured the thickness of the film simultaneously. Measurement made by the polarizer and analyzer drums of the ellipsometer were fed into an HP 85 microcomputer having an iterative programme to calculate the refractive index and film thickness.

Borosilicate glass substrates were used in this measurement for supporting the films. Three viscosities of ITO pastes were printed on the substrates. The different viscosities of the paste were identified according to the number of drops of thinner for diluting the paste, i.e. 5, 10 and 15 drops. The firing temperature was 650 °C, and the samples were fired for 30 minutes.

Transmittance, reflectance and absorbance are the most important parameters in optical properties of the film. It is hoped that the film will transmit a high level of incident light, as it is used to create the photovoltaic effect in the device. These measurements were made by using Perkin Elmer 323 Spectrophotometer. Special geometrical patterns of ITO films, i.e. (2 x 2) cm, were printed onto borosilicate glass in order to meet the requirement of the equipment. The deposition conditions were not altered, i.e. fired at 650 °C for 30 minutes in air ambient, with subsequent annealing in the vacuum.
In measuring the transmission, the 100% transmission line was checked for any obstacle in the path line for every wavelength. After checking the "0%" and "100%" chart line, the sample was then placed on the substrate holder in the compartment. The light from the beam source penetrates the film, and tracking of the transmission was carried out on the chart paper. For measuring the reflectance, an aluminium coated mirror was used as a reflectivity reference. It was assumed that the mirror reflected 100% of incident light from the beam source. After 100% chart adjustment was done, the mirror was then replaced by the substrate being measured.

5.4. INTERFACIAL LAYER OBSERVATION.

It has been previously explained that the oxide interfacial layer between the oxide semiconductor and base semiconductor is one of the major features determining the performance SIS solar cells\textsuperscript{[13-15]}. Therefore, it is essential to determine how much the SiO\textsubscript{2} exists between the film and silicon since the majority of the SiO\textsubscript{2} layer forms during cell fabrication\textsuperscript{[8,16,17]} when high temperature is applied to the silicon substrate.

A preliminary experiment consisted of depositing the ITO films, made from ESL-3050 paste, onto p-type silicon. The substrate materials used were two inch, boron doped, single
crystal silicon with (1-1-1) orientation. One side of the wafers, which was used as front surface, was optically polished. The resistivities were around 0.85 to 1.15 Ω cm and the thicknesses were around 300 μm. The two inch silicon wafers were cut into four small segments using a wafer scriber; these small segments were then used as base semiconductor substrates for supporting the ITO films.

The silicon segments were cleaned in trichloroethylene and acetone for 30 to 60 minutes in an ultrasonic cleaner. They were etched with a buffered solution of HF for a few minutes to remove any native oxides, and then rinsed with deionised water and dried by blowing argon gas at the samples. The cleaned wafer was then loaded onto the screen printer for printing. Firing was carried out at various temperature ranging from 450 °C to 650 °C in 50 °C steps. This was done in order to investigate the SiO₂ growth at elevated temperatures applied to the silicon substrates during the ITO development.

The existence of the oxide layer was observed using X-ray Photoelectron Spectroscopy (XPS). The basic principle of this method was to irradiate the sample surface by a source of low energy x-rays, generally Al Kα (1487 eV) or Mg Kα (1254 eV), under ultra high vacuum, i.e. 10⁻⁸ to 10⁻¹¹ torr, conditions.
5.5. DEVICE PREPARATION.

There were two solar cell structures made in this work. The first one consisted of an ITO films deposited straight onto the polished surface of the silicon with metal contacts on both sides of the sample. The second included a tin (Sn) metal layer between the ITO and the silicon substrate. Chemical pre-treatments for cleaning and etching on the silicon substrate were carried out, and the treatment was similar to the cleaning process described in the previous section (section V.4). A silver paste of ESL-590.G was employed for making contacts since it is the most suitable material to form a good contact with the ITO, and has been studied thoroughly for this purpose\[9\]. The front contact was in the form of grid lines and the back contact was a square pattern.

The ITO films from ESL-3050 paste were deposited on top of the polished surface of the silicon wafers to provide a transparent conductor. The printing process was adjusted in order to get the film thicknesses of around 200 to 250 nm. Firing temperatures were varied from 450 °C to 650 °C in air ambient, and the firing time was constant at 30 minutes. This was done to observe the behaviour of the device to the variation of firing temperatures. The samples were mostly annealed in the vacuum at a temperature of 300 °C for 10 minutes.

The first structure was made for a preliminary observation of the solar cell devices made by thick-film techniques. This was
discontinued since it suffered from an excessive silicon oxide growth between the ITO and silicon substrate. Moreover it gave similar results to the work done by previous workers\(^8,9,10\).

On the second structure, the fabrication technique involved three main stages of processes. After subsequent cleaning and etching, the first stage was the evaporation of aluminium on the back unpolished surface to provide an ohmic contact, and the evaporation of tin (Sn) on the front polished surface of the silicon. The source of materials of aluminium and tin were outgassed before the evaporation. A 300 nm of aluminium layer was evaporated on the back and 100 nm of tin was evaporated on the front of the silicon substrate. The pressure of the vacuum system was between $5 \times 10^{-4}$ and $2 \times 10^{-4}$ torr.

Having deposited layers of aluminium and tin, the second stage was printing the ITO-ESL 3050 paste onto the front surface, which was already covered by a tin layer, to provide a conducting anti reflection layer\(^18\). After drying, ESL 590.G silver paste was also printed on both surfaces of the substrate to aid soldering. The thickness of the silver metal layer was about 10 $\mu$m. As previously mentioned, the front contact was in the form of grid lines. This was done to reduce surface resistance, thus optimising the current transport into the load. The area covered by the grid line was about 11% of the total surface area of the device. This metal
Figure 5.7
Structure diagram of the solar cells.
(a) ITO/p-Silicon structure, (b) ITO/Sn/p-Silicon Structure.
(Drawings are not to scale).
coverage was still considered to be efficient for the front contact of the solar cell[19,20]. The device configuration is drawn in the figure 5.7.

5.6. SUMMARY.

Depositions of thin film ITO have been made in this experiment using thick-film screen printing techniques. The material used for depositing the film was a ready made ITO paste, ESL 3050. The substrates used for preliminary investigation were high grade alumina substrates, borosilicate glasses and p-type silicon wafers. A silver paste, ESL 590.G, was used for depositing metal contact. A DEK 1200 printing machine was used throughout this work. There were two choices of furnace for firing the film. These are BTU of QA Series and DEK 840. Annealing treatments were carried out in various conditions including annealing in a vacuum. This was intended to improve the electrical and optical quality of the ITO films.

Electrical characterisation was done by measuring the sheet resistance and the resistivity of the film. There were three methods of measurement employed; these were two contact method, four contact method and four point probes method. Another important measurement carried out was Hall effect measurement. For this measurement, a special film geometry was required.
Optical characterisation was achieved by measuring the transmittance, reflectance of the film since these properties are important for the application of the solar cell. The refractive index of the film was measured using ellipsometry, which simultaneously measured the thickness of the film.

The existence of an interfacial oxide layer between the ITO film and the silicon substrate was observed. This was important since the thickness of the interfacial layer would play a major role in the performance of the solar cell device. The observation was undertaken using X-ray Photoelectron Spectroscopy (XPS) method.

Successful fabrication of solar cell devices was carried out in two models. The first model was made by putting the ITO film directly on the silicon wafer. This was not further observed as it suffered from the growth of SiO₂ between ITO and Si wafers. The second model was made by inserting a tin (Sn) layer in between ITO and Si wafers. This was intended to suppress the oxide growth in order to improve the performance of the device. The average thickness of the ITO films was around 200 to 250 nm, the tin layer was about 100 nm, the evaporated aluminium was about 300 nm and the silver metal contact was about 10 μm.
REFERENCES.

CHAPTER VI.

RESULTS AND DISCUSSION.

6.1. ELECTRICAL PROPERTIES OF ITO FILMS.

One of the main materials used in this experiment was indium tin oxide prepared by depositing a ready made ITO paste using thick-film screen printing techniques. This material was variable and changed its properties depending on the treatment and conditions applied during fabrication. Preliminary investigation was made of the behaviour of the ITO film which was treated in several different ways. A series of experiments were carried out in order to provide the optimised properties of the ITO films.

Firing conditions have been the major influence in developing the characteristics of the film. As firing temperatures were varied, the sheet resistance, Rs, of the ITO films was also found to be changing dependent on the temperature being applied. It has been reported\(^1\) that a firing temperature of 650 °C for 35 minutes was the optimum firing temperature for developing the final characteristics of the films. However, a slight change in firing time was made from 35 to 30 minutes, in this experiment, as it gave better results with regard to the properties of the films. This profile was mostly used in the major characterization experiments for the ITO films.
It was found that the sheet resistance of a few kΩ/sq could easily be obtained for films prepared under optimum condition. Most of the films were deposited on high grade alumina substrates of 2"×1". The size of the printed film was 1×1 cm. The typical properties of ITO film deposited from an organometallic solutions are published by the manufacturer (i.e. ESL) as having a sheet resistance, Rs, of 1.0 ± 0.5 kΩ/sq at thickness of 250 nm, and optical transmission in the visible range is about 95%. A graph of sheet resistances (Rs) versus firing temperatures for as deposited ITO fired films printed on glass and alumina substrates is presented in Figure 6.1. The firing time was kept constant at 30 minutes.

6.1.1. The Influence Of The Annealing.

Annealing treatments were carried out in order to improve the properties of the fired ITO films. Effects of the annealing show considerable changes in the sheet resistance. A comparison of the effects of the annealing process in the oven is tabulated in Table 6.1. These results are shown graphically in Figure.6.2. Two types of the ITO paste viscosities were used i.e. undiluted and diluted with 5 drops of thinner. The firing temperature of these films varied from 600 to 650 °C inclusive increasing in steps of 25 °C.

The results showed that the temporal dependence of the resistivity during heat treatments consisted essentially of a slow transition from a room temperature to +100°C, followed by
Figure 6.1

Sheet resistance vs firing temperature for as-deposited ITO films printed on glass and alumina substrates. Four point probes and contact method were used for measuring the sheet resistance.
Graphs of annealing behaviour of the ITO films in argon ambient. (a) The ITO paste used was diluted with 5 drops of thinner. (b) The ITO paste used was undiluted. Subscript 1, 2 and 3 represent the ITO films which were fired at 600, 625 and 650 °C.
a fast transition and back to slow again at a temperature near 225 °C. Temperature annealing of 300 °C seemed to be the optimum annealing temperature, since increasing the temperature led to an increase in the sheet resistance[2,3]. Vacuum annealing, however, decreased the sheet resistance quite considerably. The sheet resistance may change by a factor of more than ten.

Table 6.1
Annealing in the oven under argon ambient.
Two types of ITO pastes were used, i.e. undiluted and diluted with 5 drops of thinner.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Paste Condition</th>
<th>Firing Conditions</th>
<th>Rs As - deposited (Kn/sq)</th>
<th>Rs After Annealing (Kn/sq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1-3</td>
<td>undiluted</td>
<td>fired at 600 °C in air</td>
<td>4.5-9.2</td>
<td>2.1-3.9</td>
</tr>
<tr>
<td>7.1-3</td>
<td>diluted</td>
<td>fired at 600 °C in air</td>
<td>4.8-10.2</td>
<td>2.9-5.0</td>
</tr>
<tr>
<td>3.1-3</td>
<td>undiluted</td>
<td>fired at 625 °C in air</td>
<td>4.3-5.6</td>
<td>1.9-2.9</td>
</tr>
<tr>
<td>8.1-3</td>
<td>diluted</td>
<td>fired at 625 °C in air</td>
<td>4.7-6.9</td>
<td>3.0-3.9</td>
</tr>
<tr>
<td>4.1-3</td>
<td>undiluted</td>
<td>fired at 650 °C in air</td>
<td>3.1-4.2</td>
<td>0.56-1.7</td>
</tr>
<tr>
<td>9.1-3</td>
<td>diluted</td>
<td>fired at 650 °C in air</td>
<td>3.7-4.7</td>
<td>0.68-1.6</td>
</tr>
</tbody>
</table>

Figure 6.3 shows the differences annealed in the oven in argon ambient or in a vacuum. The chamber pressure of the vacuum system was $10^{-5}$ Torr at the beginning of annealing and increased up to $10^{-3}$ Torr when the temperature reached 300 °C.
Figure 6.3

The difference effect of the ITO films which was annealed in the vacuum and in the oven in argon ambient. The films were fired at 650 °C for 30 minutes.
During the cooling process, the sheet resistance was considered to be constant. There was very little increase in the sheet resistance at this stage. It was believed the film activation energy was low as a very small amount oxygen diffused into the film since the annealing was in a vacuum. The results from annealing in the vacuum are recorded in Table 6.2. The contacts made for measuring the films during annealing were silver paste ESL.590.G. This paste has been studied thoroughly for this particular purpose, and it can be fired satisfactorily in quite a wide range of firing temperatures (ie.500 to 650 °C).

Table 6.2.

Annealing in a vacuum.
Three types of ITO pastes were used, i.e. diluted with 5, 10, and 15 drops of thinner and the films were fired with two types of firing ambients i.e. air and argon at 650 ° for 30 min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Paste Condition</th>
<th>Firing Condition</th>
<th>Rs As-deposited (kΩ/sq)</th>
<th>Rs After Annealing (kΩ/sq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.1-3</td>
<td>diluted with 5 drops</td>
<td>fired in air</td>
<td>3.4-4.7</td>
<td>0.27-0.32</td>
</tr>
<tr>
<td>10.1-3</td>
<td>---</td>
<td>fired in argon</td>
<td>3.1-3.6</td>
<td>0.29-0.33</td>
</tr>
<tr>
<td>21.1-3</td>
<td>diluted with 10 drops</td>
<td>fired in air</td>
<td>3.6-3.9</td>
<td>0.31-0.37</td>
</tr>
<tr>
<td>11.1-3</td>
<td>---</td>
<td>fired in argon</td>
<td>3.6-3.8</td>
<td>0.32-0.37</td>
</tr>
<tr>
<td>22.1-3</td>
<td>diluted with 15 drops</td>
<td>fired in air</td>
<td>3.7-4.2</td>
<td>0.36-0.47</td>
</tr>
<tr>
<td>12.1-3</td>
<td>---</td>
<td>fired in argon</td>
<td>3.7-3.9</td>
<td>0.39-0.45</td>
</tr>
</tbody>
</table>
Experimental data indicated that the sheet resistance of the indium tin oxide films deposited from organometallic paste gradually increased with time at room temperature. Ageing studies were, therefore, carried out in order to detect the behaviour of the resistance changes in the ITO films. These studies were based on the ITO films that had been given post deposition treatments such as annealing in the oven with argon or air ambient and vacuum annealing.

Table 6.3 shows the effect of ageing on the sheet resistance values of the films which were left in the laboratory atmosphere. The changes of the sheet resistance were recorded every day for period of ten days as shown in figure 6.4. After eight days observation, the activation energy in the film showed a reduction, and the sheet resistances tended to be established after ten days. Oxygen recaptured from the air was thought to be the cause of the increasing Rs. Voids or porosities in the printed film led to the air being captured by the film, thereby reducing oxygen vacancies in the structure, also reducing the conductivity of the film. Figure 6.5. shows the difference of the sheet resistances of the ITO films, fired at various temperatures, after ageing.

Some of the films which were deposited under the same conditions, such as firing time and temperature, showed different values of sheet resistance. These differences were possibly due to the difference in their quenched oxygen
Figure 6.4

Ageing of some typical ITO films after annealing. Samples were left in the atmosphere condition for at least 10 days.
Figure 6.5

Sheet resistance vs variation firing temperature for ITO films deposited on glass and alumina substrates. The films have been annealed in the vacuum and they were measured after ageing for at least 10 days in the atmosphere.
deficient structures. Small differences in film thickness, porosity and other process related characteristics might also have played a role.

Table 6.3.
Effect of ageing on the sheet resistance of the films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Paste condition</th>
<th>Firing Condition and treatments</th>
<th>Rs After Annealing (Ω/sq)</th>
<th>Rs After Ageing for 10 days (Ω/sq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1-3</td>
<td>undiluted</td>
<td>fired at 600 °C and annealed in the oven in argon ambient</td>
<td>2.1-3.9</td>
<td>3.2-4.5</td>
</tr>
<tr>
<td>7.1-3</td>
<td>diluted with 5 drops</td>
<td>---&quot;---</td>
<td>2.9-5.0</td>
<td>3.5-5.3</td>
</tr>
<tr>
<td>3.1-3</td>
<td>undiluted</td>
<td>fired at 625 °C and annealed in the oven in argon ambient</td>
<td>1.9-2.9</td>
<td>2.7-3.8</td>
</tr>
<tr>
<td>8.1-3</td>
<td>diluted with 5 drops</td>
<td>---&quot;---</td>
<td>3.0-3.9</td>
<td>3.4-4.3</td>
</tr>
<tr>
<td>4.1-3</td>
<td>undiluted</td>
<td>fired at 650 °C and annealed in the oven in argon ambient</td>
<td>0.56-1.7</td>
<td>1.3-2.3</td>
</tr>
<tr>
<td>9.1-3</td>
<td>diluted with 5 drops</td>
<td>---&quot;---</td>
<td>0.68-1.6</td>
<td>1.4-2.1</td>
</tr>
<tr>
<td>20.1-3</td>
<td>---&quot;---</td>
<td>fired at 650 °C in air and annealed in the vacuum</td>
<td>0.27-0.3</td>
<td>0.91-1.1</td>
</tr>
<tr>
<td>10.1-3</td>
<td>---&quot;---</td>
<td>fired at 650 °C in argon and annealed in the vacuum</td>
<td>0.29-0.3</td>
<td>0.85-0.9</td>
</tr>
</tbody>
</table>
### Table 6.3. continued

<table>
<thead>
<tr>
<th>Sample</th>
<th>Paste Condition</th>
<th>Firing Condition and Treatment</th>
<th>Rs After Annealing (KΩ/sq)</th>
<th>Rs After Ageing for (KΩ/sq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.3</td>
<td>diluted with 10 drops</td>
<td>fired at 650 °C in air and annealed in the vacuum</td>
<td>0.31-37</td>
<td>0.96-1.18</td>
</tr>
<tr>
<td>11.1-3</td>
<td>diluted with 10 drops</td>
<td>fired at 650 °C in argon and annealed in the vacuum</td>
<td>0.32-0.37</td>
<td>1.1-1.19</td>
</tr>
<tr>
<td>22.1-3</td>
<td>diluted with 15 drops</td>
<td>fired at 650 °C in air and annealed in the vacuum</td>
<td>0.36-0.47</td>
<td>1.23-1.3</td>
</tr>
<tr>
<td>12.1-3</td>
<td>&quot;-&quot;&quot;-&quot;</td>
<td>fired at 650 °C in argon and annealed in the vacuum</td>
<td>0.39-0.45</td>
<td>1.21-1.29</td>
</tr>
<tr>
<td>13.1-3</td>
<td>undiluted</td>
<td>fired at 650 °C in air and annealed in the vacuum</td>
<td>0.27-0.3</td>
<td>0.65-0.92</td>
</tr>
<tr>
<td>14.1-3</td>
<td>undiluted</td>
<td>fired at 650 °C in argon and annealed in the vacuum</td>
<td>0.28-0.3</td>
<td>0.63-0.9</td>
</tr>
</tbody>
</table>

### 6.1.3. Hall Effect Measurement.

A specific sample geometry was required for this measurement as shown in figure 5.6. A current "I" was passed through the film from opposite contacts of length of geometry. Since a specimen carrying a current I was placed in a transverse magnetic field "B", an electric field "E" was induced in the direction perpendicular to both I and B. This phenomena is known as the Hall effect. This effect allows material
characterization.

The apparatus used was designed for a sample having much lower sheet resistance value than samples in this study. Therefore, the films prepared had been treated in optimum conditions and allowed subsequent ageing in order to ensure stable properties for the measurement. The samples were placed in a magnetic flux density, B, of 0.6 Tesla, and the current, I, passed through the specimen were in the range of 0.1 to 3 mA. The Hall voltages, $V_H$, were measured using a Keithley 602 electrometer. The Hall coefficient is defined by:

$$R_H = \frac{V_H d}{I B} \quad \text{............... (6.1)}$$

$\text{d}$ is the thickness. $R_H$ is given in cm$^3$/coul. The carrier density, $N$, can be calculated from the formula -

$$N = \frac{1}{R_H q} \quad \text{............... (6.2)}$$

$q$ is an electronic charge (1.6022 x 10$^{-19}$ coul). The Hall mobility $\mu_H$ can be obtained from the equation:

$$\mu_H = R_H \times \sigma \quad \text{............... (6.3)}$$

where $\sigma = 1/\rho$, thus:

$$\mu_H = \frac{R_H}{\rho} \quad \text{............... (6.4)}$$

The best typical values of this measurement are:
\[ R_H = -2.7 \times 10^{-2} \text{ cm}^3 \text{ coul}^{-1} \]
\[ N = 2.3 \times 10^{20} \text{ cm}^{-3} \]
\[ \mu_H = 1.35 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \]

The sign showed by the Hall coefficient was negative. This determined the type of the film as n-type.

6.1.4. Thickness Measurement.

There were two apparatuses used for measuring the thickness of the films. These were a Talystep and an ellipsometer. In the Talystep, a diamond stylus with a radius of about 2.5 \( \mu m \), pressed with a 50 to 100 mg weight was drawn across the surface of the specimen. The motion of the stylus was converted to an electrical signal which was then amplified and recorded in a rectilinear recorder. There was a problem using this apparatus, in that, the substrates used for supporting the film have to be smooth, because a fairly rough substrate, i.e. alumina substrate, could lead to ambiguous results since the tip of stylus was very sensitive to an uneven surface.

Since a smooth surface of the substrate had to be used, glass substrates were then used for supporting the films. An ellipsometer was found suitable for measuring the film thickness for the film deposited on the glass substrates, since the basic method of measurement was using incident light detected by the analyzer drum. The values observed from polarizer and analyzer drums were fed to an HP 85 microcomputer. The thickness values measured with this apparatus agreed well with the measurement.
using a Talystep, and the resistivity of each of the measured films was calculated using Equation 5.6. Some thickness values and refractive indices are listed in Table 6.4. The films were treated in optimum conditions i.e. fired at 650 °C in air ambient for 30 minutes, and they were annealed in the vacuum for periods of 10 minutes.

Table 6.4.
Thickness and refractive index measurement. The films were deposited on borosilicate substrates and fired at 650 °C in air for 30 min.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Paste condition</th>
<th>Rs after vacuum annealing (KΩ/sq)</th>
<th>Thickness (microns)</th>
<th>Resistivity (Ωcm)</th>
<th>Refractive index (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.1-3</td>
<td>undiluted</td>
<td>0.27-0.31</td>
<td>0.22-0.25</td>
<td>0.6x10⁻² - 0.7x10⁻²</td>
<td>1.8</td>
</tr>
<tr>
<td>16.1-3</td>
<td>diluted with 5 drops</td>
<td>0.42-0.59</td>
<td>0.19-0.21</td>
<td>0.7x10⁻² - 1.2x10⁻²</td>
<td>1.6</td>
</tr>
<tr>
<td>17.1-3</td>
<td>diluted with 10 drops</td>
<td>0.56-0.73</td>
<td>0.17-0.18</td>
<td>0.9x10⁻² - 1.3x10⁻²</td>
<td>1.6</td>
</tr>
<tr>
<td>18.1-3</td>
<td>diluted with 15 drops</td>
<td>0.74-0.92</td>
<td>0.10-0.13</td>
<td>0.7x10⁻² - 1.2x10⁻²</td>
<td>1.4</td>
</tr>
</tbody>
</table>

6.2. DISCUSSIONS ON THE ELECTRICAL PROPERTIES OF THE ITO FILMS.

Since the material used for producing the ITO films is a ready made organometallic paste of ITO, the conductivity of the films is mostly controlled by the oxygen deficiencies or oxygen
vacancies in the structure. The vacancies are incorporated either during the film growth or after deposition by annealing in an inert atmosphere. Therefore, the firing conditions are critical in the development of the final properties of the films. For maximum conductivity in tin-doped In$_2$O$_3$, the oxygen deficient defective structures must be controlled\cite{6}. A fairly rapid cooling rate to room temperature after the film is developed at peak temperature of 550 or 650 °C, provides quenching and the oxygen deficient defective structures are trapped in the film.

The difference values of Rs samples treated in the same way might be due to the state of non-stoichiometrity which is different for every film, since the thickness of the film will not be constant (even by a few angstrom). The difference of the film thickness may affect the non-stoichiometric state\cite{7}, hence, resulting in a slight variation of the final properties of the film. The variation of sheet resistances at different firing temperatures is almost certainly due to the variation of the number of oxygen vacancies created in the films, which define the electronic conduction of the films. The results of the firing process using an argon ambient are very little different from those in air ambient. This could be happening because the argon content was not generous enough to cover the specimens during firing, therefore, there was still some air mixed in the ambient adding to the oxygen content in the films.

An experiment using some different paste viscosities was carried out to observe the variation of film thicknesses as
well as the properties for different thicknesses. The results show that adding some drops of thinner to the ITO paste affects the properties of the films. The thickness is reduced according to the number of drops of thinner used to dilute the paste. As the thickness is reduced, the sheet resistance increases and the refractive index decreases. The increase of the sheet resistance might be due to voids being created in the films which lead to oxygen recaptures by the air and thus a decrease in the conductivity. The tendency of increasing the sheet resistance when thickness is reduced agrees with the observation made by Aithchison.

Annealing of the films was the major influence on the electrical characteristics of the printed ITO films. The films included more oxygen due to the conditions of film production, annealing the films in vacuum or gas atmosphere increased the conductivity. This method induced oxygen vacancies in the structure.

The oxygen excess in the structure is probably not chemically bound in the \( \text{In}_2\text{O}_3 \) lattice doped with \( \text{Sn} \), but is dissolved as interstitial atoms or at grain boundaries. It determines the density of free electrons by acting as an electron trap. Since the oxygen excess is only weakly bound in the lattice, it is capable of easy diffusion. Therefore, upon annealing the oxygen diffuses from the interior to the surface and desorbs. If the films are exposed to the air, the diffusion goes the opposite way from the surface to the interior. This happens during ageing. The model of oxygen diffusion, absorption
and desorption seems the dominant source for the change of conductivity during annealing or ageing.

The results on annealing in argon show a decrease in the sheet resistance, hence, increasing the conductivity. However, annealing in argon is less efficient compared to annealing in a vacuum. This possibly happens because the argon activation energy seems not to be strong enough to ensure adequate desorption of the oxygen, while in the vacuum, the oxygen diffuses to the surface quite easily and desorbs from the surface into the vacuum. These results agrees with to the observation made by Hoffmann et.al\textsuperscript{9}.

6.3. OPTICAL PROPERTIES.

Films of ITO deposited from an organometallic paste have been found to have high transparency in the visible band region. This can be seen in Figure.6.6 which represents three different properties of the films. These films were fired in three different firing temperatures i.e. 450, 550 and 650 °C, and annealed in the vacuum conditions. The chamber pressure during annealing was between $10^{-5}$ to $10^{-3}$ Torr, and they were annealed for 10 minutes at 300 °C. Cooling the samples took place under vacuum. The thickness of the samples was around 230 nm, and the resistivity was $18 \times 10^{-2}$, $7 \times 10^{-2}$ and $1.8 \times 10^{-2} \Omega cm$ respectively.

It can be seen from the graph (see Fig.6.6) that, films deposited at lower temperatures have somewhat better optical transmission. The transmission in the visible region is
Transmittance and reflectance of three different ITO films. Films 1, 2 and 3 were fired at 450, 550 and 650 deg C respectively.
generally very high and the reflectivity is low. As wavelength, $\lambda$, reaches to about 1.5 $\mu$m, the reflectivity increases abruptly, causing a corresponding reduction in transmission. This is possibly because of the plasma effect resulting from the high concentration of mobility carriers. It is stated by Manifacier et al.\textsuperscript{10} that the variations in transmission are due to interference phenomena. Since the reflection indices are very high ($\approx 1.8$), reflection is the main source of light loss.

The absorption, according to Manifacier\textsuperscript{11}, is computed using the relation of $A + R + T = 100\%$. $A$ is the absorbance, $R$ is the reflectance and $T$ is the transmittance. The onset of transmission in the near UV region of about 290 nm, for the particular films, has already been found by the previous researcher\textsuperscript{1,12} for the same material and method of producing the ITO films. However if the onset of transmission is at 340 nm (see fig 6.6), a small shift in the short wavelength absorption edge is noticed. This shift depends on the firing temperatures while developing the characteristics of the ITO and subsequent annealing in the vacuum and ageing. These treatments change the electrical properties and thus change the carrier concentration, $N$. The difference in the carrier concentrations is related to the change of the shift at the onset of the transmission spectra. This shift is assumed to be due to Burstein shifts\textsuperscript{13}. This corresponds to an optical energy gap of about 4.0 eV which characterizes the ITO film as a wide bandgap material.

The determination of the fundamental absorption edge which lies in ultraviolet range has been described by the previous
researcher\[1,12\] using a relation of :-

\[ T = (1-R_A) \exp (-at) \] \hspace{1cm} (6.5)

\( R_A \) is the reflection coefficient and \( a \) is the absorption coefficient. As the extinction coefficient is much lower than refractive index \( (k^2 << n^2) \), in the absorption edge, the principal variation of \( T \) occurs in the exponential term, with \( 1-R_A \approx 1 \). Equation (6.5) then becomes :-

\[ T \approx \exp (-at) \] \hspace{1cm} (6.6)

Using this equation, the shift of the absorption edge of the film has been shown in the term of photon energy \( h\nu \), where \( h \) is Planck's constant. Figure 6.7 shows the energy dependence of \( \alpha \) for 3 ITO films with different carrier concentrations from the previous researchers\[1,12\]. This figure reveals the values of direct energy gap for films 1,2 and 3 as 3.6 eV, 3.9 eV and 4.1 eV respectively by extrapolating the linear portion of \( \alpha^2 \) vs \( h \) plot to \( \alpha=0 \). It may be noted that the fundamental absorption edge shifts from 3.6 eV to 4.1 eV may be similar to the Moss-Burstein shifts\[13,14\].

The graph of the absorption edge vs carrier concentrations made by the previous researchers\[1,12\] shows a linear relationship between \( N^{2/3} \) and the absorption edge of the film (see Fig.6.8). Using the assumption that both conduction and valence bands are parabolic the shift of \( \Delta E \) is given as in the equation :
Figure 6.7

Energy dependence of $\alpha$ for 3 ITO films of different carrier concentrations. Film 1 is unfired, film 2 is fired but unannealed, film 3 is fired and annealed. (Ref 1)
Figure 6.8

Relation of absorption edge, $E_{opt}$, of several ITO films on N. (Ref 1)
\[ \Delta E = \frac{h^2}{2m^*} \left( \frac{3N}{\pi} \right)^{2/3} \]  

(6.7)

where \( E \) is the energy in eV, \( h \) is the Planck constant, \( N \) is the carrier concentration and \( m^* \) is the effective mass. The graph in figure 6.8 can be used to estimate \( m_e \) (electron effective mass). This gives \( m_e \approx 0.80 \, m_0 \) which is comparable to values reported by other researchers\[^{15,16}\].

6.4. STRUCTURAL STUDIES.

Several ITO films were prepared for electron microscopic studies. They were deposited onto both glass and silicon substrates. Firing processes were carried out in two firing temperatures i.e. 450 °C and 650 °C for 30 minutes of firing time. The observation was made on the annealed and unannealed films. A "JOEL STEM" model "LOOCX" was used for this observation which could be used in the scanning as well as the transmission mode.

Figures 6.9 (a) and 6.9 (b) show the observation on a transmission microscope for the samples fired at 450 °C. The sample in figure 6.9(a) was unannealed film. The electrical conduction of this film is much less than that of the sample in figure 6.9(b) which was annealed in the vacuum at 300 °C for 10 minutes. The observation shows that there is no significant change in the grain structure due to annealing treatment. This is contrary to observations made by some other researchers\[^{17,18}\].
Figure 6.9 (a): TEM of ITO films fired at 450 °C (unannealed)

Figure 6.9 (b): TEM of ITO films fired at 450 °C (annealed)
Figure 6.10 (a): TEM of ITO films fired at 650 °C (unannealed)

Figure 6.10 (b): TEM of ITO films fired at 650 °C (annealed)
The same results were also found for the ITO film which was fired at 650 °C with and without annealing treatment as seen in figure 6.10 (a) and (b). However, the grain structure for the films which were fired at 450 °C, was recognised as somewhat finer when compared to the films fired at 650° C. This agrees well with the work done by other researchers\[12,20,21\] who stated that the grain size becomes larger as the temperature is increased. The increasing in the grain size is accompanied by an improvement in the electrical conduction and mobility. The typical grain size for the ITO film which was fired at 450 °C is around 150 Å and the film which was fired at 650 °C is around 200 Å.

X-ray diffraction was not undertaken in this experiment as it was expected to have the same results as obtained by previous researchers\[1,12\]. The following explanation is taken from work done by the previous researchers\[1,12\] who use the same material and method. The unfired ITO organometallic film was found to be amorphous because there were no peaks observed in the diffraction pattern (see Fig 6.11a). The fired unannealed ITO showed polycrystalline structure with random orientation. The most intense reflection, shown in figure 6.11b, is (222). The annealed ITO film has been found to have a similar diffraction pattern to the unannealed film as shown in figure 6.11c except that the annealed ITO film appears to be slightly more crystalline. The strongest peak is (222) and the second strongest is (400).
Figure 6.11

X-ray diffraction pattern for ITO on glass. The films in figure (b) and (c) were fired at 650 C. (Ref 1)
Calculations using Bragg's formula of:

\[ n \lambda = 2d \sin \theta \]

the structure of the lattice showed a simple cubic structure with a lattice constant \( a_0 = 10.0 \text{ Å} \). This compares well to the lattice constant of bulk \( \text{Sn}_2\text{O}_3 \) (\( a_0 = 10.118 \text{ Å} \))[21]. Notation in equation (6.8), \( \theta \) is the Bragg's angle, \( \lambda \) is the electron wavelength, \( n \) is a positive integer.

Comparison with the ASTM index of \( \text{SnO}_2 \) and \( \text{SnO} \) diffraction pattern does not reveal any trace of \( \text{SnO}_2 \) or \( \text{SnO} \). It is quite possible that the concentration of Sn is too low to be detected, or it might imply that the dopant Sn atoms replace indium substitutionally in the \( \text{In}_2\text{O}_3 \) lattice.

6.5. SUMMARY FOR ITO FILMS: Materials

The effects of firing temperature variation on the characteristics of ITO films have been investigated. This is one of the major influences on variation of film sheet resistance. The lowest sheet resistance was found for firing temperature of 650 °C for 30 minutes of firing time.

Firing in argon ambient was tried, and the results little improvement, being almost the same as for samples fired in air.
Annealing the film in the oven in argon ambient and in the vacuum was carried out. The sheet resistance of as-deposited ITO films showed a decrease during annealing in those ambients. Annealing in the vacuum decreased the sheet resistance more effectively than in argon; it decreased the sheet resistances by a factor of more than ten.

The Hall effect measurements show that the carriers in the ITO films are n-type. The carrier concentration obtained was \( N = 2.3 \times 10^{20} \text{ cm}^{-3} \) for the film treated in the optimum conditions and annealed in the vacuum. This indicates that the ITO films produced are degenerate semiconductors.

The thickness and refractive index of the films were measured together using an ellipsometer. Four different viscosities of the ITO paste were observed. The thickness varied from 0.1 to 0.25 \( \mu \text{m} \) and the refractive indices varied from 1.4 to 1.8. The refractive index of 1.8 was comparable with the values obtained from the films deposited using sputtering\(^{[22,23]}\).

Optical properties were observed by measuring the transmittance and reflectance of the films using a Perkin Elmer 323 Spectrophotometer. Films with three different firing temperatures, i.e. 450, 550 and 650 °C, were investigated. These temperatures determined the electrical properties of the films. The transmittance of the films exceeding more than 80%, was mostly seen in the visible band. A small shift in the short wavelength absorption edge was noticed. This was presumed to be due to the Burstein shift. The values of direct energy gaps were
quoted from the work done by previous researchers\cite{4,12}, who used the same material and method, to be 3.6 eV, 3.9 eV and 4.1 eV.

Transmission microscopy was carried out on the samples which were fired at 450 °C and 650 °C. Annealed and unannealed films for each firing temperature were observed. The grain size of the films which were fired at 650 °C was found to be slightly bigger than those of the films which were fired at 450 °C.

An X-ray diffraction results from the previous researchers showed an amorphous structure in the ITO unfired films, and polycrystalline structure with random orientation in unannealed ITO fired films. The annealed ITO fired films were found to have the same strongest peak of (222) except that the annealed films showed more crystalline features.

6.6. SOLAR CELL DEVICE PREPARATION.

6.6.1. Interfacial Layer Measurement.

It has previously been explained, in chapter 3, that the interfacial layer between oxide semiconductor and the base semiconductor is one of the major features determining the SIS or MIS solar cell performances\cite{24-27}. As far as the thick-film technique is concerned, in this present fabrication, fairly high temperatures are required in order to develop the characteristics of ITO films which have been prepared from a ready made organometallic paste. Therefore, it is very likely that the presence of an interfacial SiO₂ layer between the ITO...
and the silicon substrate is unavoidable. Moreover, ITO is an oxidizing material and can easily react with silicon to form SiO₂ or other complex oxides.

Avaritsiotis et al.[28] have studied ITO/p-Si SIS solar cells prepared using screen printing methods and have estimated an oxide layer of SiO₂ of around 20 Å. Saim et al.[1,29] found that the approximate thickness of the oxide layer, which was detected using Auger analysis, was between 60 - 100 Å. They claimed that the effect of vacuum annealing reduced the thickness of the oxide layer and improved the short circuit current of the cells.

Measurement of oxide thicknesses on bare silicon and ITO/Si structures using X-ray photoelectron spectroscopy (XPS) is presented in table 6.6. Several conditions of substrate were applied in order to see the different effect of the thicknesses. All of the substrates were precleaned before processing. The data showed that there was a slight difference in oxide thickness for the samples of bare silicon which were fired in argon and in air. On the other hand the oxide thickness looked the same if the ITO films were deposited on top of silicon substrates, and fired either in argon or in air. The firing temperature for fabricating of ITO/p-Si structures was 650 °C and the firing time was 30 minutes.
Table 6.6.

Measurement of the oxide thickness on bare silicon and ITO/p-Si structure. p-type silicon substrates were used.

<table>
<thead>
<tr>
<th>Conditions of sample</th>
<th>Oxide thickness (Angstrom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare silicon untreated (uncleaned, unfired, taken straight from the box)</td>
<td>10</td>
</tr>
<tr>
<td>Bare silicon etched with a buffer HF (unfired)</td>
<td>4</td>
</tr>
<tr>
<td>Bare silicon fired in argon at 650 °C for 30 mins</td>
<td>40</td>
</tr>
<tr>
<td>Bare silicon fired in air at 650 °C for 30 mins</td>
<td>68</td>
</tr>
<tr>
<td>ITO/p-Si structure fired in argon</td>
<td>&gt;200-250</td>
</tr>
<tr>
<td>ITO/p-Si structure fired in air</td>
<td>&gt;200-250</td>
</tr>
</tbody>
</table>

The oxide thickness of the bare silicons which were fired at the same temperature (650 °C) showed around 40 to 68 Å. Therefore, it is very likely that the ITO compounds have contributed greatly to the growth of the SiO₂ interfacial layer of the ITO/Si SIS solar cells during fabrication, as high temperature is involved.

The effect of varying temperatures on the sheet resistance of the ITO films and the oxide thickness between the ITO and silicon substrates is shown in Figure 6.12. The graph shows that at a firing temperature 650 °C, the sheet resistance, Rₛ, is approximately 1.0 kΩ/sq, and the oxide layer is extremely thick
Figure 6.12

Sheet resistance \( R_s \) and oxide thickness at various firing temperature.
(>250 Å). The thickness was appreciably decreased if the firing temperatures were reduced. An oxide thickness of around 48 Å was achieved at a firing temperature of 450 °C. However, the sheet resistance obtained was increased up to around 8 kΩ/sq. This value is considered too high to form solar cells with reasonable performance.

6.6.2. Constructing The ITO/p-Si Solar Cell.

The substrates materials were 2 inch p-type boron doped silicon wafers with (1-1-1) orientation and having resistivities of 0.85 to 1.15 Ωcm. The thickness of the wafers was around 250 to 300 μm. One side of the surface was optically polished and this was used as a front surface of the cells. The wafers were cut into four small segments using a wafer scriber. The silicon wafers were prepared by cleaning in acetone and trichloroethylene using an ultrasonic cleaner for 30 to 60 minutes, and then rinsed with deionised water. A buffer HF was used for etching the wafers to remove any native oxides or remaining dirt on the wafers. Rinsing with deionised water was again carried out after etching, and finally they were dried by blowing with argon gas. These precleaned silicon wafers were then ready to be used as base semiconductors for supporting the window conducting layer to produce solar cells.

Preliminary fabrication of the solar cell was made by placing the ITO film straight on top of the silicon wafer. The ITO film thicknesses of around 200 nm were deposited on top of smooth polished surface of the silicon wafers. The area of the
films was a square of 1x1 cm. Firing temperatures for developing the characteristics of the ITO varied from 450 °C to 650 °C inclusive in steps of 50 °C. Metalizations on the front and back contacts were made, after the ITO prints were dried, by a screen printed silver paste, ESL 590.G. The front contact was made in the form of grid lines and the back contact was a 1x1 cm square. Aluminium metal had previously been evaporated on the back surface before any of the printing processes were carried out; the thickness of evaporated aluminium was about 200 nm. This was done to produce an ohmic contact[30]. The thickness of the silver contact was about 10 μm. The sequence of processing is shown in the following diagram:

Figure 6.13.
The process sequence of the ITO/p-Si structure solar cell.

The ITO films provide a transparent conductor after firing, which would form a junction with silicon if the native oxide which had grown at room temperature did not develop further. However, the SiO₂ layer between the ITO and silicon substrate
had grown thicker during firing, as observed in the previous section. This changed the structure of the solar cell which became ITO/SiO$_2$/Si.

The characteristics of the ITO/SiO$_2$/p-Si cells were measured under dark and light conditions. The majority of the cells were found to be rectifying. The dark J-V characteristics of typical ITO/SiO$_2$/p-Si cells, representing each firing temperature are shown in Figure 6.14. The measurements were made at room temperature.

Simulated solar radiation from a tungsten halogen lamp array was used for measuring the illuminated solar cell. The array was adjusted to meet the condition of radiation of 80 mW/cm$^2$. This illumination is equivalent to air mass 2 (AM2), i.e. radiation at the surface of the earth with an illumination of 800 to 850 watt/m$^2$. The uniformity of the distributed light was estimated to be about 95%. The temperature of the samples was kept to a constant 27 °C during measurement by blowing air over the specimens using a fan.

Only the sample which was fired at 450 °C produced power under illumination. The illuminated characteristics of this particular cell are shown in figure 6.15. The properties of this cell were \( V_{oc} = 0.35 \text{ V} \), short circuit current \( J_{sc} = 0.40 \text{ mA/cm}^2 \) and fill factor \( FF = 0.37 \). The efficiency of the cell, therefore, is about \( \eta = 0.06 \% \).

The samples, which were fired at high temperatures (i.e. 500 to 650 °C), were unsuccessful and were unable to produce power under illumination. This might have happened because the
Figure 6.14

Linear dark J-V characteristics of the ITO/SiO$_2$/p-Si devices at various firing temperatures.
Figure 6.15

The illuminated characteristics of the typical ITO/SiO₂/p-Si solar cell fired at 450 °C.
interfacial layer was too large to produce the built in voltage under illumination. In the case of the sample which was fired at 450 °C, the result was quite promising. This was probably because of the interfacial layer was relatively thin. Therefore, regardless of the high value of the sheet resistance of the ITO film, the built in voltage was still created in the junction to produce the $V_{oc}$. Although the short circuit current, $J_{sc}$, was small, it was very promising in the sense that the current was still transported through the interfacial layer either by tunnelling or hopping\[^{31}\]. The suppression of the $J_{sc}$ might have been caused by the thickness of the interfacial layer, or it could have been caused by the high sheet resistance of the window layer.

6.6.3. Constructing The ITO/Sn/p-Si Solar Cell.

In the light of the previous studies on the effect of firing temperature on the creation of an oxide layer on the silicon surface, it was decided to introduce an Sn layer directly on the bare silicon surface prior to the screen printing of the ITO and subsequent firing\[^{32}\]. It was hoped that the Sn layer would act as a barrier and prevent oxidation of the silicon by the ITO during the firing process. The flow diagram process of fabricating these cells is shown in figure 6.16.
Figure 6.16.
Diagram process of the ITO/Sn/p-Si.

The device configurations of the ITO/p-Si and ITO/Sn/p-Si solar cells, which are redrawn from figure 5-7, are shown in figure 6.17. The grid line area, which covered the front surface, was about 16 mm² and this is equivalent to 16% of the surface area of the solar cell. The grid lines structure used is known as a linear grid[33]. This is the simplest grid structure for the current transport mechanism. The photogenerated current from the junction flows into the surface sheet and spreads laterally to be collected by the grid lines. It then flows through the grid lines to the collecting bus. The current flow pattern between two adjacent grid lines is shown in figure 6.18.
Figure 6.17
Configurations of heterostructure solar cells.
(a) ITO/p–Silicon, (b) ITO/Sn/p–Silicon.
Figure 6.18

Current flow pattern in the surface sheet and grid lines for the linear grid configuration. (Ref 33)
6.6.4. Results of The ITO/Sn/p-Si Solar Cells.

The device parameters of some composite cells constructed in the above manner using an additional Sn layer are listed in Table 6.7. These parameters were obtained from cells fired at a series of different firing temperatures.

### Table 6.7.
Device parameters of composite cells.

<table>
<thead>
<tr>
<th>Device no</th>
<th>Temp (°C)</th>
<th>J_{sc} (mA/cm²)</th>
<th>V_{oc} (Volt)</th>
<th>FF</th>
<th>R_s (Ohm)</th>
<th>Eff/η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTI.61</td>
<td>450</td>
<td>16.4</td>
<td>0.360</td>
<td>0.34</td>
<td>30</td>
<td>2.51</td>
</tr>
<tr>
<td>PTI.63</td>
<td>450</td>
<td>15.9</td>
<td>0.350</td>
<td>0.33</td>
<td>32</td>
<td>2.29</td>
</tr>
<tr>
<td>PTI.64</td>
<td>450</td>
<td>14.5</td>
<td>0.355</td>
<td>0.34</td>
<td>45</td>
<td>2.18</td>
</tr>
<tr>
<td>PTI.31</td>
<td>500</td>
<td>13.0</td>
<td>0.330</td>
<td>0.30</td>
<td>55</td>
<td>1.61</td>
</tr>
<tr>
<td>PTI.32</td>
<td>500</td>
<td>15.0</td>
<td>0.335</td>
<td>0.31</td>
<td>45</td>
<td>1.95</td>
</tr>
<tr>
<td>PTI.33</td>
<td>500</td>
<td>14.5</td>
<td>0.327</td>
<td>0.31</td>
<td>50</td>
<td>1.84</td>
</tr>
<tr>
<td>PTI.35</td>
<td>500</td>
<td>14.5</td>
<td>0.340</td>
<td>0.32</td>
<td>45</td>
<td>1.97</td>
</tr>
<tr>
<td>PTI.71</td>
<td>550</td>
<td>4.5</td>
<td>0.250</td>
<td>0.21</td>
<td>92</td>
<td>0.30</td>
</tr>
<tr>
<td>PTI.72</td>
<td>550</td>
<td>4.8</td>
<td>0.275</td>
<td>0.27</td>
<td>90</td>
<td>0.45</td>
</tr>
<tr>
<td>PTI.73</td>
<td>550</td>
<td>3.5</td>
<td>0.275</td>
<td>0.25</td>
<td>98</td>
<td>0.30</td>
</tr>
<tr>
<td>PTI.74</td>
<td>550</td>
<td>4.2</td>
<td>0.260</td>
<td>0.25</td>
<td>94</td>
<td>0.34</td>
</tr>
<tr>
<td>PTI.41</td>
<td>600</td>
<td>0.43</td>
<td>0.196</td>
<td>0.20</td>
<td>120</td>
<td>0.02</td>
</tr>
<tr>
<td>PTI.42</td>
<td>600</td>
<td>0.35</td>
<td>0.186</td>
<td>0.20</td>
<td>125</td>
<td>0.016</td>
</tr>
<tr>
<td>PTI.45</td>
<td>600</td>
<td>0.27</td>
<td>0.228</td>
<td>0.19</td>
<td>130</td>
<td>0.014</td>
</tr>
<tr>
<td>PTI.51</td>
<td>650</td>
<td>0.30</td>
<td>0.158</td>
<td>0.19</td>
<td>132</td>
<td>0.011</td>
</tr>
<tr>
<td>PTI.52</td>
<td>650</td>
<td>0.17</td>
<td>0.188</td>
<td>0.19</td>
<td>137</td>
<td>0.007</td>
</tr>
</tbody>
</table>

(1) R_s is the series resistance of the device.

Figures 6.19(a-d) show the characters of those parameters listed in table 6.7. As seen in Figure 6.19a, the increase of the firing temperature leads to a decrease in the efficiency. It is obvious that the high firing temperature process may cause the oxide layer to become thicker even with an Sn layer present.
Figure 6.19 (a) : Efficiency vs temperature.

Figure 6.19 (b) : Fill factor vs temperature.
Figure 6.19 (c) : Short circuit current density vs temperature.

Figure 6.19 (d) : Open circuit voltage vs temperature.

Figure 6.19 (e) : Series resistance vs temperature.
Therefore, it is very difficult for the current to tunnel through the interface\(^{[24,34]}\). In figure 6.19b, the fill-factor tends to decrease with an increase in the temperature and the same occurrence also happens in the \(J_\infty\) and \(V_\infty\) (see figure 6.19c,d). The drop in the efficiency can be thought of as due to an increasingly effective series resistance as the tunnelling current changes exponentially with the thickness of the layer. It can be seen in figure 6.19e that the series resistance increases as the firing temperature is increased.

Two typical illuminated characteristics of the ITO/Sn/p-Si solar cells are presented in figures 6.20(a,b). These were obtained from cells which were fired at 450 °C and 500 °C respectively. It can be seen that the softness of knee of the \(J-V\) characteristics suggests photocurrent suppression effects\(^{[35]}\).

Dark \(J-V\) characteristics were measured using a Hewlett Packard (4145.B) semiconductor analyzer. Supposing thermionic emission to be the majority current, then the current density \(J\) across the barrier will be given by\(^{[36]}\)

\[
J = A^*T^2 \exp\left(-\frac{q\phi_b}{kT}\right) \left\{ \exp\left(\frac{qV}{nkT}\right) - 1 \right\} \quad \ldots \ldots \quad (6.9)
\]

Substitution \(J_o = A^*T^2 \exp\left(-\frac{q\phi_b}{kT}\right)\) \quad \ldots \ldots \quad (6.10)

\[
\therefore \quad J = J_o \left\{ \exp\left(\frac{qV}{nkT}\right) - 1 \right\} \quad \ldots \ldots \quad (6.11)
\]

For \(V \gg kT/q\),

\[
J = J_o \exp\left(\frac{qV}{nkT}\right) \quad \ldots \ldots \ldots \quad (6.12)
\]
Figure 6.20

Typical illuminated characteristics of ITO/Sn/p-Si solar cells.
(a) PTI-35 device fired at 500 °C, with \( V_{oc} = 0.340 \) V, and \( J_{sc} = 14.5 \) mA/cm\(^2\). (b) PTI-61 device fired at 450 °C, with \( V_{oc} = 0.360 \) V and \( J_{sc} = 16.4 \) mA/cm\(^2\).
where $A^{**}$ is the effective Richardson constant, $T$ is the temperature (in K), $V$ is the applied voltage, $n$ is the ideality factor, $\phi_b$ is the barrier height, and $kT/q$ is the thermal voltage ($\approx 0.0258$ V at 300 K).

In order to determine the barrier height and the ideality factor, equation (6.12) can be expressed as

$$\ln(J) = \ln(J_o) + qV/nkT \quad \ldots \ldots \ldots \ldots \ldots (6.13)$$

Equation (6.13) implies that a plot of $\ln(J)$, as a function of $V$, should result in a straight line, having a slope $q/nkT$ and intercept $\ln(J_o)$. However, for sufficiently small and sufficiently large currents the linear relationship does not hold\[35\], but is generally quite accurate over many orders of magnitude of current.

Figures 6.21(a,b) show the J-V curves plotted as $\ln(J)$ vs applied voltage, $V$. Calculations using equation (6.13) from the tangential slopes shown in figures 6.21 gives $n$ values between 2.1 to 4.0. It was found by Card et.al\[42\] that an increase of $\text{SiO}_2$ in silicon Schottky barrier devices led to an increased value of $n$. The short-circuit photocurrent, electrons from the ITO layer, was expected to tunnel through the insulator ($\text{SiO}_2$).

The electrons might recombine with light-generated current giving rise to photocurrent suppression. The barrier height from equation (6.10) gives a range of values for $\phi_b$ between 0.64 to 0.74 eV. These values are considered to be as expected for thermionic emission\[37\]. The high current part of the J-V plot
Figure 6.21

In J-V curves of ITO/Sn/P-Si in the dark condition. (a) PTI-61 device fired at 450 °C, (b) PTI-35 device fired at 500 °C. Ideality factors found were 2.1 and 4.0 respectively.
shows the effect of the series resistance as a limitation to the ideal behaviour.

The current transport may not however be entirely due to tunneling. Other mechanisms such as field emission\textsuperscript{[24,34]}, thermally enhanced emission, multistep tunnelling, trapping and subsequent emission could be involved in the device\textsuperscript{[38]}.

In order to examine the nature of the barrier at the interfaces, it is useful to analyze the junction capacitance as a function of a bias voltage. The junction capacitance of the ITO/Sn/p-Si device can be measured by superimposing a small ac voltage of about 5 mV on the dc bias. The frequency of the ac signal used was 1 MHz. The dc biases were applied between the device electrodes. For a given value of this bias, a definite charge distribution in the system will arise. The differential capacitance as a function of dc bias can then be determined. The resulting capacitance vs voltage curve can be compared with a calculated curve or one analyzed from a system which has a similar structure. The relationship between C and V obtained is shown in figure 6.22.

Figure 6.23 shows that a plot of $1/C^2$ vs bias voltage is linear, although there is a slight shift from this relation at a high applied voltage. Thus the capacitance varies inversely as the square root of applied reverse bias voltage. This linearity indicates an abrupt junction, and implies that a single potential barrier exists only at the surface of the
Figure 6.22

Junction capacitance vs bias voltage for sample PTI-61, measured by superimposing a 5 mV ac signal (frequency 1 MHz) on the reverse dc bias.
Figure 6.23

The relationship between $1/C^2$ and the reverse dc bias for sample PTI-61. Built in potential obtained from this curve is $V_d = 0.62$ Volt.
silicon\textsuperscript{[39-41]}. Therefore, the ITO/Sn/p-Si device can be treated in accordance with the analyses of the system which have similar structures such as metal-insulator-semiconductor (MIS) or Schottky barrier devices.

The diffusion potential or built in potential obtained from the intercept absissa in the plot of $1/C^2$ vs bias voltage, $V$, is $V_d = 0.62$ Volt. This is measured at room temperature ($\approx 298$ K). Doping concentration in the silicon can be calculated using the following equation\textsuperscript{[41]}:

$$\frac{1}{C^2} = \frac{2}{q \varepsilon_n \varepsilon_0 N_A A^2} (V + V_d) \quad \ldots \ldots \ldots (6.14)$$

where $\varepsilon_n$ is the relative permittivity of the semiconductor, $\varepsilon_0$ is the permittivity of free space, $A$ is the surface area, $V$ is the reverse bias voltage and $V_d$ is the built in voltage. From the slope of $1/C^2$ vs bias voltage, $V$, calculated by using the equation written above (6.14), the doping concentration of the p-type silicon substrate is found to be $N_A = 5.99 \times 10^{15}$ cm$^{-3}$.

6.7. SUMMARY OF THE SOLAR CELL FABRICATION.

Measurement of the interfacial layer between the ITO and silicon substrate was carried out, since the layer one of the major problems of determining the performance of the device\textsuperscript{[35,37,43]}. Measurements were made of the oxide thickness of bare silicons and in the structure of the ITO/silicon. Firing
temperatures were varied, on the observation of the ITO/Si structure, from 450 °C to 650 °C in steps of 50 °C. It was found that the oxide thickness in the ITO/Si structure, which was fired at 650 °C, was more than 250 Å, and the oxide thickness of the structure which was fired at 450 °C was about 48 Å. The graph of the compensation of the sheet resistance and the oxide thickness versus temperature is presented in figure 6.12.

A preliminary fabrication process of the solar cell by placing the ITO film straight on top of the polished surface of p-type silicon, i.e ITO/p-Si structure, had been suggested and tried by the previous researchers[1,28,29]. Similar results were again obtained. The majority of the cells were found to be rectifying. However, they were hardly producing any power when illuminated, except the structure which was fired at 450 °C. The poor power production was thought to be due to the SiO₂ layer which had grown between the ITO and silicon substrate.

Having evaluated the effects of the oxide layer in the structure above, it was decided to make a slight alteration in the structure[32]. A thin Sn layer was introduced directly on top of the polished silicon surface prior the screen printing processes. There were two expectations from inserting the Sn layer in the structure; one was to suppress the oxide growth by the silicon during processing, the other was to increase the conductivity of the window layer. The results of the ITO/Sn/Si structure were significantly improved compared to the previous structures.
Logarithmic J-V curve measurements were made using a Hewlett Packard (4145.B) semiconductor analyzer. From these curves, the ideality factor, $n$, of the devices was calculated, and they gave the range of $n$ values between 2.1 to 4.0.

The junction capacitance of the ITO/Sn/p-Si structure was measured as a function of a bias voltage. The plot of $1/C^2$ versus bias voltage was found to be linear. This linearity indicated an abrupt junction and implied that a single potential barrier exists only at the surface of the silicon.
REFERENCES.

CHAPTER VII.

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK.

7.1 INTRODUCTION.

Firstly, this chapter outlines the major achievements of this work. These are:

1. The poor performance of ITO/p-Si structure solar cells made by thick film deposition has been investigated and found to be due to the thickness of the oxide layer.

2. ITO/Sn/p-Si heterostructure solar cells have been successfully fabricated using screen printed ITO on an evaporated Sn on a p-type silicon wafer. Results of the solar cell properties presented in this thesis are encouraging.

3. Optimum processing conditions for fabricating ITO/Sn/p-Si have been found in terms of firing temperature and annealing.

Secondly, it then makes more detailed comments on the materials study and on fabrication techniques for the solar cell studied.

Finally, suggestions are made as to how the work should be continued.
7.2. CONCLUSIONS ON THE MATERIAL STUDIES.

Transparent semiconducting films of ITO were deposited on to some substrates, i.e. alumina, glass and silicon, using the screen printing method. Some experimental treatments were carried out on the ITO, in the preliminary investigation, in order to find the best properties of the films. The development of the properties of the ITO films required firing. Therefore variations of firing temperatures were made to discover the optimum temperature for the best development of these properties, e.g. the sheet resistance of a few \( \Omega/\text{sq} \) can easily be obtained for as-deposited film which is fired at 650 °C for 30 minutes.

It is suggested that the conduction mechanism in the transparent semiconductor oxide films involves stoichiometric relationship or incorporation of impurities\(^1\). Therefore, presence of defects resulting from the non-stoichiometry of the material are thought to be the origin of the conductivity.

The annealing process significantly improved the electrical properties of the films. The sheet resistance of a few \( \Omega/\text{sq} \) of as-deposited film was reduced to a few hundred \( \Omega/\text{sq} \) after annealing. Annealing processes were done in two environments; that is annealing in argon in the oven, and annealing in the vacuum as suggested by Molzen\(^2\) and Siuta et.al\(^3\). This method induced oxygen vacancies in the film, thus lowering the resistivity of the film. The decrease in the resistivity when the sample was annealed in vacuum or in argon atmospheres, could be due to the oxygen diffusion from the interior to the surface and
desorption. This created oxygen vacancies in the lattice. The reduction in resistivity after annealing of the ITO films, prepared by sputtering, was also observed by other researchers. This was explained as due to increase in degeneracy of the film with heat.

The carrier concentrations type of the ITO film, showed by the Hall measurement, was n-type (electrons). The electron concentration obtained from this measurement was about $N_e = 2.3 \times 10^{20}$ cm$^{-3}$.

Grain sizes of the ITO, fired at 450 °C and 650 °C, have been found to be slightly different. However there was no significant change detected in the grain size between annealed and unannealed films fired at the same temperatures. The grain size of the film which was fired at higher temperature was found to be slightly bigger, and this agreed well with the work done by others. The range of the grain sizes was about 100 to 150 Å.

The lattice constant for this particular film was estimated by the previous researchers to be $a_0 = 10.00$ Å. The SnO$_2$ or SnO phases was not clearly traced in the structure. This implied the tin concentrations could be very small, or they might replace indium substitutionally in the In$_2$O$_3$ lattice and produce a non-stoichiometric condition. X-ray diffraction studies done by the same authors revealed that the structure was polycrystalline with (222) and (400) peaks.

Being a transparent oxide semiconductor, the transmittance of the ITO films was shown to exceed 80%. This was found mostly
in the middle of the visible band. Reflectance showed an increase when the wavelength reached the IR region. As a transparent material with a high conductivity, ITO is very useful in solar cell applications, particularly as a transparent conducting window layer.

7.3. CONCLUSIONS ON THE SOLAR CELL FABRICATION.

Transparent oxide films of ITO have been successfully deposited onto silicon wafers using thick-film screen printing techniques. These films act as window conducting layers in ITO/p-Si and ITO/Sn/p-Si structures of solar cells. The first structure which had been suggested by previous researchers\[8-10\] was made as preliminary research. This was abandoned as it suffered from excessive oxide thickness between the ITO film and the silicon.

The interfacial layer measurement showed that the oxide layer (SiO₂) had grown greatly at various firing temperatures i.e. 450 °C to 650 °C. The thickness of the oxide layer was found to be extremely thick (> 250 Å) at a high firing temperature (650 °C) and it decreased as the firing temperatures were reduced. The oxide thickness of around 48 Å was obtained at a firing temperature of 450 °C. This temperature was considered to be acceptable for fabricating the solar cell, even though the sheet resistance was found to be high (≈ 8 KΩ/sq).

In view of the previous observations on the effect of firing temperatures on the creation of the oxide layers (SiO₂), it was decided to introduce an Sn layer directly on top of the bare
silicon prior to screen printing of ITO. The insertion of the Sn layer altered the structure which then become ITO/Sn/p-Si. By inserting the Sn layer, it was hoped that the growth of the oxide ($\text{SiO}_2$) could be suppressed. Also the conductivity of the window layer would be increased.

Having experience of the results obtained from this structure, it implied that the oxides still grew inevitably at elevated temperatures of processing, resulting in alteration of this particular solar cell to become a multistructure of ITO/Sn/$\text{SiO}_2$/p-Si. Temperature processing at 450 °C and 500 °C has produced encouraging results. The oxide thicknesses grown at these temperatures were estimated in the range of 40 to 60 Å. However, the general results showed improvements compared to the previous structure.

The short circuit current densities were increased from $J_{sc} = 0.73$ to 0.75 mA/cm$^2$ obtained by the previous researchers$^{[8-11]}$ to $J_{sc} = 13.0$ to 16.4 mA/cm$^2$. However, the open circuit voltage obtained was somewhat lower $V_{oc} = 0.360$ Volt. This may have come from recombination through interface states due to the lattice mismatch$^{[12]}$. The fill factors found were also low, $FF = 0.19$ to 0.34. These were thought to be due to series resistance of the device being rather high ($\approx 35$ ohm). In addition, it was also likely that the large value of thicknesses of the interfacial layer may have reduced the value of fill factor as stated by Shewchun et al$^{[13]}$. 
The ideality factor, $n$, was observed for a typical device fired at 450 °C to be 2.1. It was found by Card et al.\textsuperscript{14} that an increase of SiO$_2$ thickness in silicon Schottky-barrier devices led to an increased value of $n$. $n$ value greater than unity are associated with thermionic emission\textsuperscript{15}.

The small signal capacitance-voltage (C-V) characteristics are very useful in obtaining the potential barrier at the junction. The $1/C^2$ versus $V$ plot, where $C$ is the junction capacitance, is linear. This indicates an abrupt heterojunction with uniform acceptor concentration in the silicon. A single potential barrier exists in the silicon surface and no barrier in the ITO/Sn region. Thus it can be considered that the capacitance of an Si-Sn/ITO heterostructure comes from a depletion layer in the silicon surface.

7.3. SUGGESTIONS FOR FUTURE WORK.

1. The ITO films produced in this experiment were made from ready made organometallic pastes manufactured by the ESL company, in which the concentration of the composition of indium and tin dissolved in the ITO mixture were not entirely known. The experiment showed that the SnO$_2$ or SnO were untraceable which implied that the concentration of Sn could be very low. Therefore, it is advisable to study further the composition of the ITO paste since it is known that the Sn concentration of 5 to 9 wt % has been proved to have reasonable electrical, optical and physical properties.
2. It is known that different methods of deposition can produce different film properties. The research could, therefore, be very useful if it started by varying the relative amount of indium, tin and oxide in the paste in order to obtain optimum properties of the ITO films prepared by the screen printing method.

3. A study on the evaporated Sn film could be extended in terms of thickness, electrical and optical properties to obtain the best characteristics of the film. Investigation of the interface between ITO and Sn, also between Sn and silicon is highly recommended. This would lead to an improve understanding to the ITO/Sn/p-Si structure.

4. One of the major problems in this work is lowering the open circuit voltage in the device, hence, lowering the efficiency of the solar cell. This may have come from the thickness of the insulating layer being rather high. Therefore, lower fabricating temperatures are suggested i.e. < 450 °C, in order to further reduce the thickness of the insulating layer. This will require modification of the paste. Verification of the form of the junction and the transport mechanisms operative in this particular solar cell is necessary. This is useful to clarify the idea of the current transport in the device and gives more understanding to the operative limitations of the device.

5. Study on the interface states which are present between the interfacial oxide and the two semiconductors, i.e. ITO on
the top end and silicon at the bottom end, could be very useful to determine the performance of the device, since these interface states will affect the ideal characteristics of the device.
REFERENCES.


APPENDIX


"COMBINATIONS OF EVAPORATION AND SCREEN PRINTING TECHNIQUES FOR FABRICATING ITO-TIN (Sn)-P TYPE SILICON SOLAR CELLS"
COMBINATIONS OF EVAPORATION AND SCREEN PRINTING TECHNIQUES
FOR FABRICATING ITO - TIN (Sn) - p TYPE SILICON SOLAR CELLS.

R.MULYADI and D.S.CAMPBELL.
Department of Electronic and Electrical Engineering,
University of Technology, Loughborough,
Leicestershire, LE 11 3 TU, England - UK.

ABSTRACT.

Combinations of evaporation and thick-film screen printing techniques were used for fabricating indium tin oxide (ITO) - tin (Sn) - p-type silicon heterostructure solar cells. A 100 nm tin layer was evaporated onto the front surface of p-type silicon substrates and screen printed ITO was deposited on top of the tin layer. These substrates were then fired for 30 minutes at various firing temperatures ranging from 450 °C to 650 °C inclusive-increased in steps of 50 °C.

The ITO film, in this structure, acts as a conducting window layer. Optical measurements show that they are highly transparent in the visible band region, and the electrical properties show that they are reasonably conductive. The sheet resistance of the ITO films is about 290 ohm/sq, measured during annealing in vacuum condition at temperature of 300 °C and gradually increases after ageing for a few days in atmosphere conditions. Typical values obtained for these cells are an open circuit voltage, Voc= 0.360 volts, a short circuit current density, Jsc = 16.4 mA/cm² with a fill factor, FF = 0.34 and efficiency of about, = 2.5 % under 80 mW/cm² simulated illumination. This illumination is equivalent to air mass 2 (AM 2), i.e. radiation at the surface of the earth with an illumination of 800-850 watt/m².
Solar cell devices of semiconducting oxide deposited on a bulk semiconductor have been attracting considerable attention in the past few years. These devices have resulted from an effort to find alternatives to the conventional p/n junction solar cells which have already been established. Tin oxide (SnO$_2$), indium oxide (InO$_2$) and indium tin oxide (In$_{1-x}$Sn$_x$O$_{2-y}$; commonly termed ITO) are examples of the common semiconducting oxides that are being extensively investigated for the fabrication of solar cells.

Heterojunctions and SIS heterostructures are the common models for fabricating solar cell devices using such material, where each of them has their own advantages. Various techniques used for depositing such films onto a semiconductor have been established. Thick film screen printing techniques have been used by previous workers[1,2,3] for depositing the ITO organometallic paste onto silicon substrates as a conducting window layer to produce solar cells. The window permits the transmission of solar radiation directly onto the active substrate with little attenuation. Spray deposited ITO on n-type silicon have yielded solar cell efficiencies, $\eta$, up to 12%[4,5].

It has been established that a very thin insulator interfacial layer between the oxide semiconductors and the base semiconductors is very critical[6,7]. This ultra thin layer can be used to modify the barrier and transport properties of the junction. The silicon dioxide grown on the silicon during processing at elevated temperatures is found to act as a satisfactory interfacial layer provided it is thin enough.
This paper describes the research done into the fabrication of solar cells using screen printing thick film techniques. Organometallic ITO was printed onto silicon substrates which were fired at various firing temperatures ranging from 450 to 650 °C for a period of 30 minutes. It was found that SiO₂ layers grew as sandwiches between the ITO and the silicon during firing. The thickness of the silicon-oxides was observed to be increased by high firing temperatures. It was thus decided to put a Sn layer on top of the silicon substrates before the ITO layer was printed\(^{[20]}\). This layer was used to suppress the growth of the silicon oxides during processing.

The organometallic paste (resinate) to produce the ITO film is manufactured by Electro Science Laboratory (ESL) and consists of indium and tin compounds dissolved homogeneously in a viscous organic liquid. This rheology makes it suitable for application for screen printing. When printed onto a substrate and fired in air, the organic constituents of the printed layer decompose, leaving a thin film of indium tin oxide firmly bonded to the substrate. Screen printing and evaporation of the films were both used alternately during fabrication.

Results of an experimental study of heterostructure solar cells comprising of ITO and Sn films deposited on p-type Si substrates will be discussed.

2. DEVICE PREPARATION.

The fabrication technique used for these particular solar cells include three main stages of process. The first one is the evaporation of aluminium on the back surface of the silicon to provide ohmic contact, and the evaporation of tin on the front
polished surface of the silicon substrates. The second is printing ITO-ESL 3050 paste onto the front surface which acts as a conducting antireflection layer. Silver from ESL (type 590 G) is also printed on the back and front surface of the substrates to aid ease of soldering. On the front surface, the silver paste is printed in the form of grid lines. This aims to reduce surface resistance, thus optimising the current transport into the load. The final process is firing in a moving belt furnace in order to develop the electrical and optical properties of the ITO films.

A number of two inch single crystal p-type silicon wafers having resistivities of 0.85-1.15 ohm cm were prepared by cleaning and etching, and they were used as substrates. The orientation of the wafers was (1-1-1) with the thickness around 250 μm. The two inch silicon wafers were cut into smaller segments which were then used as base semiconductor substrates for supporting the tin and ITO in order to construct the solar cells. The physical structure for the ITO-Sn-p-type silicon solar cell is schematically drawn in Fig.1.

Chemical pre-treatments for cleaning and etching the substrates were carried out. The substrates were ultrasonically cleaned in warm trichloro-ethylene and acetone for a few minutes followed by etching in a buffer HF solution to remove the native oxide layer from the silicon. After rinsing in de-ionized water and drying, the wafers were immediately put into a vacuum evaporator for evaporating the aluminium and tin.

The sources of the materials, aluminium and tin, were outgassed before the evaporation. A 300 nm layer of aluminium was evaporated on the back unpolished surface and 100 nm of tin was evaporated onto the front polished surface of the silicon wafers.
The pressure of the vacuum system was between $5 \times 10^{-6}$ and $2 \times 10^{-4}$ torr.

Having deposited a layer of aluminium and tin by evaporation, the substrates were then loaded on to a screen printer, and ITO paste was then printed on top of the tin layer, and dried at a temperature of 130 °C for 10 minutes. The screen printer machine (DEK 1200) was adjusted in order to give an average fired film thickness of about 200 nm. After printing the ITO, silver paste (ESL 590 G) was printed on both sides of the substrates. A grid line pattern was printed onto the top surface, and a square pattern, (1 x 1) cm, on the back surface. Finally, the substrates were fired in a moving belt furnace. The firing temperatures were found to be suitable for the aluminium alloying on the back surface used to provide ohmic contact\cite{21}. Moreover, these were also applicable for firing silver paste, giving a layer which showed good adhesivity to the substrates and satisfactory physical and electrical properties.

3. RESULTS AND DISCUSSION.

3.1. Material Studies.

A series of experiments was carried out to provide some values of the properties limiting the performance of solar cells. Firing conditions have been the major influence in the developing of the electrical characteristics. It has been stated by Saim et.al\cite{2,3} that a firing temperature of 650 deg C for 35 minutes is the optimum condition to develop electrical characteristics of ITO.
Borosilicate glass substrates were used for observing the optical properties of the film, and high grade alumina substrates for the electrical properties. Characterization results achieved had similar values to those obtained by previous workers\textsuperscript{[2,3]} which were carried out on printing, firing and annealing of the ITO films. However, in the present case the firing time had been reduced slightly to 30 minutes. As an example transmittance of the films was found to be exceeding more than 80% at illumination wavelength $>$400 nm (see Fig.2.).

Annealing of the fired ITO films in a vacuum chamber at 300°C for 10 minutes at peak temperature decreased the sheet resistance by a factor of more than ten. Final values of $\approx$ 300 ohm/sq have been obtained. However, the sheet resistance was found to slightly increase after the films were taken out from the vacuum chamber. Oxygen recaptured could be the cause of this increase of the sheet resistance\textsuperscript{[8]}. The sheet resistance values were found to finally stabilize at around $\approx$ 1 Kohm/sq after subsequent ageing in air for a few days.

Observation on the growth of the SiO$_2$ was done on silicon-ITO structure. Although the native oxide layer on the silicon had been previously removed by etching in buffered HF solution, the SiO$_2$ layer was still, inevitably, forming between the ITO film and the silicon substrates during the firing process. It has been stated by Thompson et.al\textsuperscript{[6]}, that the SiO$_2$ might be formed by oxygen reduction of the ITO by the silicon, since the ITO can be considered to be an oxidizing material. Moreover, porosities in the films might be holding oxygen, hence contributing to the production of the oxide growth.

Measurement of oxide thickness on silicon, using x ray
photoelectron spectroscopy (XPS), is presented in Table 1. The basic principle of the measurement is that of irradiating the sample surface by a source of low energy X rays, AlKα (1487 eV) under ultra-high vacuum (10⁻⁸ - 10⁻¹¹ torr). Several preparation conditions for the substrates were used in order to observed the difference of oxide thickness obtained.

**Table 1.**

**Measurement of the oxide thicknesses of silicon**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Condition of sample</th>
<th>Oxide thickness (Ångstrom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-type Si</td>
<td>Bare silicon untreated</td>
<td>10</td>
</tr>
<tr>
<td>p-type Si</td>
<td>Bare silicon etched with buffer HF</td>
<td>4</td>
</tr>
<tr>
<td>p-type Si</td>
<td>Bare silicon etched and fired in argon at 650 °C for 30 minutes.</td>
<td>40</td>
</tr>
<tr>
<td>p-type Si</td>
<td>Bare silicon etched and fired in air at 650 °C for 30 minutes.</td>
<td>68</td>
</tr>
<tr>
<td>p-type Si</td>
<td>ITO printed on the Si, fired in argon at 650 °C for 30 minutes.</td>
<td>&gt;200-250</td>
</tr>
<tr>
<td>p-type Si</td>
<td>ITO printed on the Si, fired in air at 650 °C for 30 minutes.</td>
<td>&gt;200-250</td>
</tr>
<tr>
<td>p-type Si</td>
<td>ITO printed on the Si, fired in air at 450 °C for 30 minutes.</td>
<td>48</td>
</tr>
</tbody>
</table>

Figure 3 shows that the silicon dioxide in the Si-ITO structure is getting thicker for higher firing temperatures, and thinner at low temperatures. Also shown in Fig.3 is the effect of firing temperature on sheet resistance and it can be seen that
although a low firing temperature gives a thin oxide, the sheet resistance is high (≈ 8 Kohm/sq). The lowest firing temperature used is thought to be the minimum firing temperature required for developing the characteristics of the ITO films\textsuperscript{[10]}.

In the light of the above studies on the effect of firing temperature on the creation of an oxide layer on the silicon surface, it was decided to introduce an Sn layer directly on top of the bare silicon surface prior to the screen printing of the ITO and subsequent firing\textsuperscript{[20]}. It was hoped that the Sn layer would act as a barrier and prevent oxidation of the silicon by the ITO during the firing process. The results obtained using such a composite will be discussed in the following section.

3.2. Device Studies.

The device parameters of some composite cells constructed in the above manner using an additional Sn layer are listed in Table 2. These parameters were obtained from cells fired at a series of different firing temperatures.

Table 2.

Device parameters of composite cells

<table>
<thead>
<tr>
<th>Device no</th>
<th>Temp (°C)</th>
<th>Jsc (mA/cm(^2))</th>
<th>Voc (Volt)</th>
<th>FF</th>
<th>Rs(^{(1)}) (ohm)</th>
<th>Eff/(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTI.61</td>
<td>450</td>
<td>16.4</td>
<td>0.360</td>
<td>0.34</td>
<td>30</td>
<td>2.51</td>
</tr>
<tr>
<td>PTI.63</td>
<td>450</td>
<td>15.9</td>
<td>0.350</td>
<td>0.33</td>
<td>32</td>
<td>2.29</td>
</tr>
<tr>
<td>PTI.64</td>
<td>450</td>
<td>14.5</td>
<td>0.355</td>
<td>0.34</td>
<td>45</td>
<td>2.18</td>
</tr>
<tr>
<td>PTI.31</td>
<td>500</td>
<td>13.0</td>
<td>0.330</td>
<td>0.30</td>
<td>55</td>
<td>1.61</td>
</tr>
<tr>
<td>PTI.32</td>
<td>500</td>
<td>15.0</td>
<td>0.335</td>
<td>0.31</td>
<td>45</td>
<td>1.95</td>
</tr>
<tr>
<td>PTI.33</td>
<td>500</td>
<td>14.5</td>
<td>0.327</td>
<td>0.31</td>
<td>50</td>
<td>1.84</td>
</tr>
<tr>
<td>PTI.35</td>
<td>500</td>
<td>14.5</td>
<td>0.340</td>
<td>0.32</td>
<td>45</td>
<td>1.97</td>
</tr>
<tr>
<td>PTI.71</td>
<td>550</td>
<td>4.5</td>
<td>0.250</td>
<td>0.21</td>
<td>92</td>
<td>0.30</td>
</tr>
<tr>
<td>PTI.72</td>
<td>550</td>
<td>4.8</td>
<td>0.275</td>
<td>0.27</td>
<td>90</td>
<td>0.45</td>
</tr>
<tr>
<td>PTI.73</td>
<td>550</td>
<td>3.5</td>
<td>0.275</td>
<td>0.25</td>
<td>98</td>
<td>0.30</td>
</tr>
<tr>
<td>PTI.74</td>
<td>550</td>
<td>4.2</td>
<td>0.260</td>
<td>0.25</td>
<td>94</td>
<td>0.34</td>
</tr>
</tbody>
</table>
Table 2, continued.

<table>
<thead>
<tr>
<th>Device no</th>
<th>Temp (°C)</th>
<th>$J_{sc}$ (mA/cm²)</th>
<th>$V_{oc}$ (Volt)</th>
<th>FF</th>
<th>$R_s$ (*) (ohm)</th>
<th>Eff/η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTI.51</td>
<td>650</td>
<td>0.30</td>
<td>0.158</td>
<td>0.19</td>
<td>132</td>
<td>0.011</td>
</tr>
<tr>
<td>PTI.52</td>
<td>650</td>
<td>0.17</td>
<td>0.188</td>
<td>0.19</td>
<td>137</td>
<td>0.007</td>
</tr>
</tbody>
</table>

*)$R_s$ = series resistance of the device.

The illuminated characteristics of the cells were measured under a solar simulator using a halogen lamp array. The array was adjusted to meet the condition of radiation of 80 mW/cm² which is comparable to the average of solar spectrum at the earth surface (AM2). The temperature of the samples was kept down to a constant 27 °C during measuring by blowing air over the specimens using a fan.

As seen in Table 2, the increase of firing temperature leads to a decrease in the efficiency. It is obvious that the higher firing temperature process may cause the oxide layer to become thicker even with an Sn layer present. Therefore, it is very difficult for the current to tunnel through the interface\(^{[7,11]}\). Two typical illuminated characteristics are presented in Figure 4. These were obtained from cells which were fired at 450 °C and 500 °C respectively.

Dark J-V characteristics were measured using a Hewlett Packard (4145.B) semiconductor analyser. Supposing thermionic emission to be the majority current, then, the current density $J$ across the barrier will be given by\(^{[12]}\):

$$J = A^* T^2 \exp \left( -\frac{q\phi_b}{kT} \right) \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] \ldots (1)$$
Substitution \[ J_o = A'' T^2 \exp \left( -\frac{q\phi_b}{kT} \right) \] \hspace{1cm} \text{.........(2)}

\[ J = J_o \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] \] \hspace{1cm} \text{.........(3)}

For \( V \gg kT/q \),
\[ J = J_o \exp \left( \frac{qV}{nkT} \right) \] \hspace{1cm} \text{.........(4)}

where \( A'' \) is the effective Richardson constant, \( T \) is the temperature (in K), \( V \) is the applied voltage, \( n \) is the ideality factor, \( \phi_b \) is the barrier height, and \( kT/q \) is the thermal voltage (\( \approx 0.0258 \) V at 300 K). In order to determine the barrier height and ideality factor, equation (4) may be expressed as :

\[ \ln J = \ln (J_o) + \frac{qV}{nkT} \] \hspace{1cm} \text{.........(5)}

Equation (5) implies a plot of \( \ln (J) \) as a function of \( V \) should result in a straight line, having a slope \( q/nkT \) and intercept \( \ln (J_o) \). However, for sufficiently small and sufficiently large currents the linear relationship does not hold\([13]\), but is generally quite accurate over many orders of magnitude of current. Figure 5, shows the J-V curves plotted as \( \ln (J) \) vs applied voltage, \( V \). Calculation using equation (5), from the tangential slopes shown in Fig.5 gives \( n \) values between 2.1 - 4.0, and the barrier height calculated from equation (2) gives a range of values of \( \phi_b \) between 0.64 - 0.74 eV. These values are considered to be as expected for thermionic emission\([13]\). The high current part of the J-V plot shows the effect of the series resistance as a limitation to ideal behaviour.
The current transport may not however be entirely due to thermionic emission. Other mechanisms such as tunnelling or field emission\cite{7,11}, thermally enhanced emission, multistep tunnelling, trapping and subsequent emission can be involved in the device\cite{14}.

In order to examine the nature of the barrier at the interfaces it is useful to analyse the junction capacitance as a function of bias voltage. The junction capacitance of the ITO-Sn-p silicon device can be measured by superimposing a small ac voltage ($\approx 5$ mV) on the dc bias. The frequency of the ac signal used was 1 MHz. The dc biases were applied between the device electrodes.

For a given value of this bias a definite charge distribution in the system will arise. The differential capacitance as a function of dc bias can then be determined. The obtained capacitance vs voltage curve can be compared with a calculated curve or one analyzed from a system which has a similar structure. The relationship between $C$ and $V$ obtained is shown in Figure 6.

Figure 7 shows that a plot of $1/C^2$ vs bias voltage is linear, although there is a slight shift from this relation at high applied voltage. Thus the capacitance varies inversely as the square root of applied reverse bias voltage. This linearity indicates an abrupt junction, and implies that there exists a single potential barrier only at the surface of the silicon \cite{15,16,17}. Therefore, the ITO-Sn-p silicon device can be treated in accordance with the analyses for metal-insulator-semiconductor (MIS) or Schottky barrier devices.
The diffusion or built-in potential obtained from the intercept absissa in the plot of \(1/C^2\) vs. \(V\) is \(V_b = 0.62\) Volt. This is measured at room temperature (\(\approx 298\) K). Doping concentration in the silicon can be calculated using the equation as follows[17]:-

\[
1/C^2 = \frac{2}{q \varepsilon_r \varepsilon_0 N_s A^2} \left( V + V_d \right) \quad \ldots \ldots \ldots \ldots (6)
\]

where \(\varepsilon_r\) is the relative permittivity for semiconductor, \(\varepsilon_0\) is the permittivity of free space, \(A\) is the surface area, \(V\) is the reverse bias voltage and \(V_d\) is the built in voltage. From the slope of \(1/C^2\) vs \(V\) calculated by using the equation written above (6), the doping concentration of the p-type silicon substrate is found to be \(N_s = 5.9 \times 10^{15} \text{ cm}^{-3}\).

4. CONCLUSION.

Transparent semiconductor films of ITO have been deposited as a transparent conducting layer for ITO-Sn-p type silicon structure solar cells by using screen printing techniques. The insertion of a tin (Sn) layer in between the ITO and silicon was decided on after a series of oxide (\(\text{SiO}_2\)) thickness measurements had been made at various firing temperatures and conditions. The tin layer appears to suppress the growth of the oxide layer on the silicon during fabrication.

Devices prepared at processing temperature of 450 °C and 500 °C gave encouraging results with efficiencies up to 2.5 %. The
oxide thicknesses grown at these particular temperatures were estimated to be in the range of 40-60 Å. The short circuit current densities obtained have been increased from values of \( J_{sc} = 0.73-0.75 \, \text{mA/cm}^2 \) obtained by previous workers\(^2,3\) to \( J_{sc} = 13.0 - 16.4 \, \text{mA/cm}^2 \). However, the open circuit voltage obtained was somewhat lower at \( V_{oc} = 0.360 \, \text{Volt} \). This may have come from recombination through the interface states due to the lattice mismatch\(^{18}\). The fill factors found were also low, \( FF = 0.19-0.34 \). These were thought to be due to the series resistance of the devices being rather high ( \( \geq 30 \, \text{ohm} \))\(^{18}\). In addition, it was also likely that the large value of thicknesses of the interfacial layer may have reduced the value of the fill factor as stated by Schewchun et al\(^{18}\).

The ideality factor, \( n \), was observed for a typical device fired at 450 °C to be \( n = 2.1 \). It was found by Card and Rhoderick\(^{19}\) that an increasing of \( \text{SiO}_2 \) thickness in silicon schottky-barrier devices leads to increasing value of \( n \). The \( n \) value greater than unity, stated by Ghosh et al\(^{13}\), is associated with thermionic emission. This can be attributed to a combination of oxide thickness and surface density of states.

The linearity of \( 1/C^2 \) vs \( V \) where \( C \) is the junction capacitance indicates that the silicon substrate has a uniform doping concentration. A single potential barrier exists in the silicon surface and no barrier in the ITO/Sn surface. Thus it can be considered that the capacitance of an Si-Sn/ITO heterostructure comes from a depletion layer in the silicon surface.
ACKNOWLEDGMENT.

The authors wish to thank Dr. A. Subrahmanyam for many helpful discussions, and his contribution to the process technology.
REFERENCES.

10. Detail specification of ESL-3050 paste (ITO) from the manufacturer.
Figure 1.
Structure diagram of ITO-Sn-silicon solar cell. (Drawing is not to scale.)

Figure 2.
Transmittance and reflectance of ITO film in the visible band region. The film was fired at 650 deg C for 30 minutes, and annealed in vacuum for 10 minutes at a temperature of 100 deg C.
Figure 1.
Sheet resistance and oxide thickness at various firing temperatures.
Typical illuminated characteristics of ITO-Sn-p silicon solar cells. (a) PTI-61 device fired at 450 deg C, with Voc = 0.360 V and Jsc = 16.4 mA/cm². (b) PTI-35 device fired at 500 deg C, with Voc = 0.340 and Jsc = 14.5 mA/cm².

In J-V curves of ITO-Sn-p-silicon solar cells in the dark condition. (a) PTI-61 device fired at 450 deg C. (b) PTI-35 device fired at 500 deg C. Ideality factors found were n = 2.1 and 4.0 respectively.
Figure 6.
Junction capacitance vs. bias voltage for sample PTI-61 measured by superimposing a 5 mV ac signal (frequency 1 MHz) on the reverse dc bias.

Figure 7.
The relationship between $1/C^2$ and the reverse dc bias for sample PTI-61. Built-in potential obtained from this curve is $V_d = 0.62$ Volt.
THE END
APPENDIX


"COMBINATIONS OF EVAPORATION AND SCREEN PRINTING TECHNIQUES FOR FABRICATING ITO–TIN (Sn)–P TYPE SILICON SOLAR CELLS"