ELECTRICAL AND OPTICAL CHARACTERIZATION OF FLUORINE - DOPED ZINC OXIDE THIN FILMS DEPOSITED BY SPRAY PYROLYSIS TECHNIQUE

BY

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A thesis presented to Kenyatta University, in partial fulfilment of the requirement for the degree of Master of Science in Physics of Kenyatta University.

DECEMBER, 1996.
DECLARATION

I hereby declare that this thesis is my original work and has never been presented in any University for the award of a degree.

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This thesis has been submitted for examination with our approval as University supervisors.

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DEDICATED TO
MY LATE PARENTS SILVANCE WERE AND PELESIA ANYANGO

who have been a great source of inspiration to me in my endeavor to explore the frontiers of
science in the service of mankind.
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"You O sun, are the eye of the world
You are the soul of the embodied beings
You are the source of all creatures
You are the discipline of all engaged in work".

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ABSTRACT

The electrical and optical characterization of transparent and conducting Zinc Oxide and Fluorine doped Zinc oxide thin films, deposited by spray pyrolysis technique are presented. The optimum conditions for deposition have been established. The effects of air and vacuum annealing on electrical and optical properties of undoped ZnO and Fluorine doped ZnO films were investigated. Air annealing showed an increase in sheet resistance of the films while vacuum annealing showed a decrease in sheet resistance of the films. After annealing in vacuum, the sheet resistance for the best deposited film was found to be in the range of 270 - 300Ω. The thermoelectric power investigations of the doped ZnO films showed that the charge carriers were electrons (n-type). The activation energies obtained for differently doped films were in the range of 0.47 - 0.65eV. Direct band gap of ZnO films was found to be 3.24eV. The highest transmittance obtained was about 82%. An attempt was made to fabricate ZnO : F / SiO₂ / p-Si solar cell which yielded an open circuit voltage of 0.235V, short circuit current density of 1.41mA / cm², fill factor of 0.267 and efficiency of 0.11%. The low efficiency could be attributed to thick interfacial oxide layer.
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CHAPTER ONE
INTRODUCTION

Spray deposited Zinc oxide materials for solar cells look promising in the field of solar photovoltaic (PV) research for the conversion of solar energy into electrical energy. In the spray process, many factors affect the quality of the films such as the substrate temperature, spray rate, the pressure of the carrier gas and the height of the spray. The spray pyrolysis lends itself ideally to production of extremely durable metal oxide based coatings by deposition onto the surface of a hot glass. Multilayer deposition is also possible. Zinc oxide is promising in the field of solar cells because of its good electrical and optical properties and its conductivity can be manipulated by controlling deviations from the stoichiometry and doping effects. A specific and important advantage of the doped oxide semiconductor are their excellent chemical and mechanical durability, which allows their use on glass surfaces exposed to the air. The purpose of this work is to present a basic study of the electrical and optical properties of the spray deposited zinc oxide thin films doped with Fluorine for use as a window material for solar cells.

1.1 SOLAR ENERGY

The growing worldwide demand for energy, its increasing cost and the depletion of fossil fuel energy reserves have accelerated research into renewable energy sources. Solar energy is a potential candidate for new energy [1]. Energy resources that are not derived from solar energy are nuclear, geothermal and tidal energy.

Several methods of utilizing solar energy are being used or tested today and others are on the drawing board. Utilization of solar energy can be divided into two categories. These are photovoltaic and photothermal. In photovoltaic, sunlight is directly converted to electricity by using the photovoltaic effect. Photons incident on a semiconductor surface generate electron - hole pairs. These pairs are separated by an internal electric field across the solar cell junction which produces an electric current in the external circuit. In the photothermal approach, incident light is absorbed by the absorber surface to generate heat. This surface in a solar absorber should have high solar absorptance and low thermal emittance to suppress thermal radiation losses [2].
In both the photovoltaic and photothermal systems, the optical properties of the surface have a significant effect on the systems performance. Widespread utilization of solar energy requires development of durable, low cost, optically efficient solar selective coatings and producing inexpensive, efficient and reliable solar cell.

The research and development in the field of photovoltaic energy conversion is currently directed towards:

◊ developing materials of improved characteristics,
◊ developing manufacturing techniques which are expected to reduce the manufacturing cost of solar cells and
◊ improving the conversion efficiency of thin film solar cells.

Optical films have received considerable attention in research and development in the last forty years. Photovoltaic has been emphasized by solid state physicists and material scientists as opposed to the development of selectively absorbing films with solar absorptance and low thermal emittance. In addition to solar absorbers, other optical films are required in photothermal converters. Reflector materials are needed in concentrating collectors. Transparent conducting materials are essential as front electrodes on schottky - barrier and metal insulator semiconductors (MIS) photovoltaic devices. Ultraviolet reflecting or absorbing interference filters protect plastic glazings and encapsulants from photo degradation.

The complete optical characterization of thin films require measurement of the spectral bi-directional reflectance and transmittance from 0.35 to 30 µm over all angles of incidence. The basis of energy conversion is the absorption of photons by the semiconductor. Only photons of the appropriate energy can be absorbed by the material. It is therefore important to look at the spectrum of the sunlight, specifying number of photons for each energy wavelength.
1.2 SOLAR RADIATION

The radiation energy output from the sun originates from nuclear fusion reaction. About $6 \times 10^{11}$ kg/s hydrogen is converted into helium with a net loss of about $4 \times 10^3$ kg, which is converted into energy ($4 \times 10^{20}$ J). This energy is emitted as electromagnetic radiation in the ultraviolet to infrared region (0.2 to 3.0 μm). The total mass of the sun is now estimated at $2 \times 10^{20}$ kg and radiates energy output of over 10 billion joules [3].

The temperature of the center of the sun is of the order $10^6$ Kelvin but the surface temperature is approximately 6,000 K. The spectrum of the sunlight approximates that of a black body radiation at this temperature. The absorption by the atmosphere is different for different wavelengths, hence the solar spectrum on the earth is different in intensity and shape to that emitted by the sun. The absorption in the ultraviolet is due to electronic transitions in molecular and atomic oxygen, nitrogen and ozone in the upper atmospheric layers. Water vapour and carbon dioxide molecules are responsible for the absorption bands in the infrared. Scattering of the radiation in the atmosphere is responsible for diffuse component, along with the direct radiation component coming directly from the sun. The spectral distribution of the diffuse light differs from that of direct light, generally it is relatively richer in the higher energy or blue wavelengths [4].

The power density associated with solar radiation on a plane perpendicular to the direction of the sun at the mean earth sun distance, outside the earth's atmosphere is called the solar constant (its value is 1.37 KWm$^{-2}$). The radiation is referred as the air mass zero (AM0) radiation. Sunlight is attenuated during its passage through the earth's atmosphere. The attenuation depends on the distance to be covered. Since the spectra distribution also depends on the attenuation, several solar spectra can be considered, depending on the length of the light path through the atmosphere. This light path is shortest when the sun is at the zenith. The air mass is the ratio of the actual path length of the solar radiation through the atmosphere to its minimum value. When the sun is at the zenith the air mass is one (AM1). When the solar radiation makes an angle $\theta$ with the zenith the air mass is given by,

$$\text{Air mass} = (\cos \theta)^{-1}$$  \hspace{1cm} (1)
Figure 1.1 The spectrum of sunlight. The different curves refer to the black body radiation at 5762K (broken line), the AM0 spectrum (outside the earth's atmosphere) and the AM1 spectrum [4].
The higher the air mass, the stronger the attenuation of the light. The spectral distribution of the solar radiation is also a function of the air mass as indicated in figure 1, where commonly used air mass spectra are represented.

AM1.5 is the spectrum of the "standard sunlight". It corresponds to an angle of 48.2° in equation (1), which can be considered as a typical value. The maximum power density received at the earth's surface is about 1,000 Wm⁻².

1.3 TRANSPARENT CONDUCTORS AND ANTI-REFLECTION COATINGS

Transparent conducting semiconductors permit light transmission and at the same time they are effectively metals. They have a wide band gap and they are generally oxides. Transparent and conducting films have featured prominently for many years in a wide variety of applications, such as heating elements on aircraft windows for deicing and defogging, antistatic coatings on instrumental panels and electrical contacts in liquid crystal electrochromic and electroluminescent displays. The high reflection in the infrared region, in conjunction with high transparency in the visible region, has been exploited to make heat reflecting mirrors.

The desired properties of a transparent conducting film are a high band gap, above 3.0 eV, a low effective mass of charge carriers and high carrier mobility. The most commonly used transparent conducting oxide films are those of tin oxide, indium oxide and cadmium tin oxide. They must be degenerately doped so as to resemble metals. The refractive index of these materials is such that they can be used as partial anti-reflecting coatings. Anti-reflecting coatings are generally added to the surface of a solar cell to minimize surface reflections and to increase absorption.
1.4 APPLICATION OF OPTICAL FILMS

1.4.1 Introduction

In discussing low temperature applications of optical films, the electromagnetic spectrum can be split into the solar region (0.25 - 2.5 µm) and the thermal infrared region (2.5 - 30 µm). Four independent parameters can be used to define optical performance:

- the solar reflectance \( \rho_s \) and transmittance \( \tau_s \),
- the thermal reflectance \( \rho_t \) and transmittance \( \tau_t \).

Ideal optical materials are those for which absorption \( \alpha \) (\( \varepsilon \)), reflectance and transmittance approach extremes of 1 and 0 independently in the solar and thermal infrared spectral regions. The solar absorptance \( \alpha_s \) and the normal thermal emittance \( \varepsilon_t \) can be defined as follow:

\[
\alpha_s + \rho_s + \tau_s = 1 \quad \text{(2)}
\]
\[
\varepsilon_t + \rho_t + \tau_t = 1 \quad \text{(3)}
\]

Detailed discussions of the optical properties and measurements appropriate for solar applications are presented by Touloukian [5] and Masterson et al [6].

Although considerable work remains to improve the optical properties, cost and durability of films for particular application, much emphasis is laid on refining present materials and techniques. A research direction is towards developing switchable materials. A window coating for example, might be switched from a heat mirror state \( \tau_s = 1 \) for winter use to solar shade \( \tau_s = 0.3, \rho_s = 0.7 \) to limit summer time cooling loads.
1.4.2 Anti-reflecting coatings

The surface reflection of light as it encounters a change in index of refraction at the boundary between two materials can be a critical loss in solar applications such as glazings, photovoltaics and absorber surfaces. At normal incidence the surface reflectance is given by,

\[ R = \frac{[( \eta_1 - \eta_2 )^2 + ( k_1 - k_2 )^2 ]}{[( \eta_1 + \eta_2 )^2 + ( k_1 + k_2 )^2 ]} \]  

(4)

where \( \eta \) and \( k \) are the real and imaginary components of the complex index of refraction \( \eta' = \eta + ik \) for materials 1 and 2 on either side of the interface. \( R \) is approximately 0.04 for a glass-air interface. For high index of refraction materials such as semiconductors losses in excess of 0.35 can be expected if no attempt is made to reduce the surface reflectance. Coatings or treatments for reducing the surface reflectance loss are called anti-reflecting layers. They are formed by interposing a layer of intermediate index of refraction between the high and low index materials. The simplest technique consist of depositing an anti-reflecting layer of index of refraction \( \eta \) and thickness determined by [7],

\[ d = \frac{\lambda}{4\eta} ; \quad \eta = (\eta_1\eta_2)^{1/2} \]  

(5)

where \( \lambda \) is the wavelength corresponding to the minimum desired surface reflectance.

A variety of inorganic dielectrics deposited by sputtering, evaporation, glow discharge, chemical vapour deposition and thermal oxidation have been explored as potential anti-reflecting coatings.
1.4.3 Heat mirrors

Heat mirrors are films that possess a high infrared reflectance and low infrared emittance. For solar applications a second constraint is placed on the desired material (high solar transmittance). Heat mirrors may be incorporated into greenhouse glazings and architectural windows to enhance thermal gain of the structures. Applications to flat plate, evacuated tube or solar pond heat collectors allow good optical selectivity without placing stringent thermal stability requirements on the material. Alternatively, heat mirrors may be applied directly to an absorbing surface to form an inverted tandem stack such as tin oxide doped with fluorine on black enamel [8]. An indirect application of heat mirrors to solar energy technologies occurs in the processing of materials such as semiconductors for photovoltaic devices in high temperature furnaces where a heat mirror may greatly enhance energy efficiency of the processing step without compromising visual access [9].

The materials of interest in solar applications are of three types: thin metallic films, conducting metallic oxides and multilayer stacks. Thin metallic films of interest have been Cu, Ag and Au, all of which have high IR reflectance and relatively good transmittance in the solar spectrum. Heavily doped SnO₂, In₂O₃ and metallic oxides ReO₃, NaₓWO₃ and Cd₂SnO₄ have been investigated as heat mirrors [10].

1.4.4 Transparent conducting electrodes (TCE)

Since the electronic properties of a material determining the infrared (IR) reflectance also are involved in defining the electronic conductivity, the materials previously considered as heat mirrors are also of interest as TCE's. In addition to the optical properties, the thin-film electrical sheet resistance and the interface resistance between the underlying electrode and the semiconductor substrate are parameters of interest for TCE's. The boundary resistance is particularly sensitive to the defect density at the interface and thus deposition conditions and
material compatibility are critical. Vossen [11] has extensively reviewed these conditions, concluding that extreme variations in electrical properties can be reported for nominally similar materials, and careful study of thin microstructure and impurity concentrations is needed to define an electrode material. As an example for a specific material, Fan et al [12] reported the importance of controlling the oxygen pressure during vapour deposition on tin-doped indium oxide. Analogous to the situation for absorber materials (where reductions in solar absorptance represent a irretrievable loss to the system but increased thermal emittance can be partially compensated for in system design), the solar transmittance of TCE is fundamental parameter of concern, and the electrical properties of a film may be partially compensated for by device design [13]. Other applications for TCE may be found in large area switchable devices e.g., as electrodes for electrochromic or liquid critical materials in switchable solar shades.

1.5 LITERATURE REVIEW

Transparent conducting oxides are widely used in various fields [14]. Potential use of transparent conducting oxides as solar cell electrodes has renewed research interest on these films, from the possibility of fabricating large-area, stable and efficient solar cells utilizing these films. Various techniques have been employed to deposit these films from which various physical properties for application have been investigated. The techniques include sputtering [15, 16], ion planting [17], spray pyrolysis [18, 19], chemical vapour deposition [20, 21], reactive evaporation [22] and anodization [23]. The physical properties include structural, electrical and optical properties.

The most established and well studied transparent conducting oxides are indium tin oxide and fluorine doped tin oxide films. The increasing use of transparent conductors in various fields have prompted interest in the study of the physical properties of zinc oxide films. This is because zinc oxide has a wide band gap ($E_g = 3.3$ eV) and its conductivity can be manipulated by controlling deviations from the stoichiometry and doping effects [24]. Recent work on the
deposition of ZnO films by sputtering [15, 16], reactive evaporation [22], spray pyrolysis [18, 19] and chemical vapour deposition [20, 21] has yielded films with optical transmittance of about 80 - 90% in the visible region and electrical resistivity in the range of $10^{-3} - 10^{-2} \, \Omega \, \text{cm}$.

Among these physical and chemical deposition techniques [25], spray pyrolysis is more advantageous. This technique presents a convenient technological method for fabrication of low cost solar cells. This method also lends itself ideally to the production of extremely durable transparent oxide based coatings by deposition onto the surface of a hot glass. Multilayer deposition is also possible. It was used as early as 1910 to obtain transparent oxide films. In 1960's Chamberline et al [26] extended the technique to sulfide and selenide films. The major challenge to preparing high quality films by spray pyrolysis is to minimize the high porosity and gross texturing that is associated with volume shrinkage and the evolution of gaseous by-products.

Aranovich et al [19} presented a more detailed analysis of the structural, electrical and optical properties of spray deposited ZnO films. These films exhibit a wurtzite structure with the c-axis normal to the substrate. On doping with indium, the ZnO films deposited by spray pyrolysis show random orientation of the 200 - 400Å crystallite [27]. The electrical properties of spray deposited films are strongly influenced by the substrate temperature and the rate of air flow. As-deposited films have a high resistivity of about $10^2 \, \Omega \, \text{cm}$, which decreases to about $10^3 \, \Omega \, \text{cm}$ on annealing in vacuum [27] or H$_2$ [19]. The change in resistivity is mainly due to the variation in mobility [27].

Recently, large-area ZnO films have been prepared by spray pyrolysis [28], with low resistivity ($\approx 8 \times 10^{-4} \, \Omega \, \text{cm}$), high electron concentration ($\approx 5 \times 10^{20} \, \text{cm}^{-3}$) and electron mobility of about 15 cm$^2$V$^{-1}$s$^{-1}$. S. Major et al [18] have prepared indium-doped zinc oxide films using the technique which exhibited attractive transparent conducting properties. Typically a film 8000Å thick had a visible transmittance of about 85% and an electrical resistivity of about $8 \times 10^{-4} \, \Omega \, \text{cm}$. They also studied the annealing effects on the electrical properties of the films in vacuum, oxygen and air ambients. J. Goyal et al [29] have deposited Al:ZnO films using the same technique which exhibited conductivity of $50 \, \Omega \, \text{cm}^{-1}$ which can be increased further by the
annealing. These results show that ZnO closely rivals the established and well studied indium tin oxide and fluorine doped tin oxide films.

Since the renewed research interest on transparent conductors stems from the possibility of fabricating large area, stable and high efficiency solar cells, it is important to discuss solar cells as well. The photovoltaic effect was discovered by Edmond Becquerel in 1839. He noted that a voltage was developed when light was directed into one of the electrodes in an electrolyte solution. The effect was first discovered in solid in 1877 by W. G. Adams and R. W. Day [30], who conducted experiments with selenium. In 1954, researchers turned to the problem of utilizing photovoltaic effect as a source of power. High efficiency solar cell was first developed by Chapin, Fuller and Pearson using a silicon p-n junction [31]. Development have been going on in different parts of the world to improve the efficiency and minimizing fabrication cost.

Many materials have been studied for thin film solar cells. Thin film solar cells and tandem structures made from polycrystalline compound semiconductors provide high efficiencies (12% with CuInSe₂) with improved stabilities [32]. Among the most promising photovoltaic thin film generator which have been widely investigated is CdS-Cu_xS [28]. For the heterojunction system CdS-Cu_xS, conversion efficiencies as high as 9% have been reported [35]. Recently G. Sassi [33] proposed cascade composition layers. The new design adds other useful benefits to the advantage of both cascade systems and graded gap regions. A. Rockett et al [34] have reviewed the properties and most successful methods of producing CuInSe₂ films for solar cell application. He noted the most successful methods are three source elemental evaporation and selenization of Cu / In layers in H₂Se atmospheres. Devices based on CuInSe₂ have achieved the highest conversion efficiencies for non epitaxial thin film solar cell; 14.1% for small cell and 10.4% for 3914 cm² device.

A wide range of thin film solar cells already exists in the market. This includes the heterojunction p-i-n junction, schottky barrier the metal - insulator - semiconductor (MIS) and the metal - oxide - semiconductor (MOS) cells [35]. The main disadvantage of thin film solar cells is the low efficiencies obtained. This is due to the grain boundary effects and the poor quality of the semiconducting material that often results from growth upon foreign substrates.
1.6 OBJECTIVES OF THE PRESENT WORK

The objectives of this work are:

1. To study the effects of Fluorine doping and annealing on the electrical and optical properties of zinc oxide films deposited by spray pyrolysis technique.

2. To establish the deposition parameters which yield highly transparent and conducting ZnO films using this technique.

3. An attempt to fabricate solar cell using Fluorine - doped ZnO film from which efficiency and fill factor will be determined.
CHAPTER TWO

THEORY

2.0 INTRODUCTION

The choice of correct semiconductor material in both photovoltaic and photothermal systems is very important for efficient and stable performance. Some of the important properties that help in choosing a material for a particular utilization are: Structure, optical and electrical properties of the material. It is therefore important to discuss the factors which influence these properties. Several semiconductors used in photovoltaic (PV) application include tin oxide, indium oxide, indium tin oxide and zinc oxide. In this work, we limit our discussion to zinc oxide.

2.1 ZINC OXIDE

Zinc oxide crystallizes in the hexagonal wurtzite lattice in which the oxygen ions are arranged in closest hexagonal packing and the zinc ions occupy half of the tetrahedral interstitial positions with the same relative arrangement as the oxygen ions [36]. The lattice is shown in figure 2.1. The lattice parameters are $a = 3.24 \text{ Å}$, $c = 5.19 \text{ Å}$, the ratio $c / a = 1.60$.

The environment of each ion does not have the exact tetrahedral symmetry. Instead, the spacing between the nearest neighbours in the direction of the hexagonal or c-axis is smaller than for the other three neighbours. The binding is essentially polar, however, there is a homopolar component of binding between next nearest zinc and oxygen ions in the direction of the c-axis [37]. Zinc oxide is an n-type wide gap semiconductor. It has a band gap of 3.33 eV. This band gap allow zinc oxide to be transparent in the entire visible region of the spectrum. The electrical and optical properties have been investigated by various authors [18, 19, 29], and results show that ZnO can be used as a transparent conducting material.
Figure 2.1: The wurtzite structure of zinc oxide.

- oxygen
- zinc
2.2 BAND GAP.

The electrons of isolated atoms have well defined discrete energy levels. In solid materials in which the atoms are close to each other and interact, the individual levels spread out to form bands. For electronic photovoltaic and photothermal applications, the major bands are the conduction and the valence band separated by energy gap. The difference between the bottom of the conduction band and the top of the valence band edge is called band gap. The best values of band gap are obtained by optical absorption. In a crystal, photon absorption can take place in two processes; direct and indirect.

2.2.1 Direct band gap

Consider the band structure of semiconductors i.e the energy - momentum (E - K) relationship of the electrons in the semiconductor, which is fundamental to an understanding of the electrical and optical properties. The simplest form of the energy band in a crystal consists of a parabolic conduction band with a minimum at K = 0, and both bands with spherical energy surfaces. This type of structure is shown in figure 2.2. The lowest point of the conduction band occurs at the same value of K as the highest point of the valence band. A direct optical transition is drawn vertically with no significant change of K, because the absorbed photon has a very small wave vector. The threshold of continuous optical absorption at frequency \( \omega \_g \) determines the band gap \( E_g = h \omega _g / 2\pi \) in figure 2.2. In the direct absorption process, a photon is absorbed by the crystal with the creation of an electron and a hole.

2.2.2 Indirect band gap

Most real crystals have much more complex structures. Energy extrema for electrons in the conduction band and holes in the valence band are at different points in the K - space. This structure is shown in figure 2.3. In the indirect absorption process, the minimum energy gap of the band structure involves electrons and holes separated by a substantial wave vector \( K_c \). Here a direct transition at the energy of the minimum gap cannot satisfy the requirement of conservation of
Figure 2.2: The simplest form of band structure in a solid with parabolic conduction and valence band with extrema at $K = 0$. 
Figure 2.3: Indirect band gap.
wave vector because photon wave vectors are negligible at the energy range of interest. But if a

These equations are called Fresnel coefficients. At angles of incidence $\theta_1$ and refraction $\theta_2$, $r$ and $t$ depends on the polarization of the incident wave. For a wave with electric vector in the plane of incidence,

phonon of wave vector $K$ and frequency $\Omega$ is created in the process, then we have,

$$K (\text{ photon}) = K_c + K \cong 0 \quad \text{--------------------------------- (6)}$$

$$\frac{\hbar \omega_g}{2\pi} = E_g + \hbar \Omega / 2\pi \quad \text{--------------------------------- (7)}$$

as required by the conservation laws.

The intrinsic conductivity and intrinsic concentrations are largely controlled by $E_g / K_B T$, the ratio of band gap to the thermal energy. When this ratio is large, the concentration of intrinsic carriers will be low and the conductivity will be low. This implies that the band gap may also be deduced from the temperature dependence of the conductivity or of the carrier concentration in the intrinsic range. Optical measurements are used to determine whether the gap is direct or indirect.

2.3 ABSORPTION IN SEMICONDUCTORS

The ability of a material to absorb light of a given wavelength is described by the absorption coefficient $\alpha(\lambda)$. The incident light inside a semiconductor falls off in intensity by $1/e$ for a distance $1/\alpha$. Hence the absorption coefficient can be used to determine the thickness of the semiconductor material used for complete absorption of light.

For a semiconductor in which the minimum of the conduction band and the maximum of the valence band occur at the same value of $K$, electron - hole pair generation begins at $h\nu = E_g$ and the electron is transferred vertically between the two bands without a change in momentum. Non vertical transitions are normally forbidden in this case. The optical absorption coefficient for a direct transition is given by [38],

18
\[ \alpha = A \left( \frac{E_g}{hv} \right)^{1/2} \]  

where for allowed transitions,

\[ A = 3.38 \times 10^7 \eta^{-1} \left( \frac{m_e}{m_0} \right)^{1/2} \left( \frac{E_g}{hv} \right) \]

where \( m_0 \) is the free electron mass, \( m_e \) is the mass of electron, \( v \) is the frequency of the radiation and \( \eta \) is the refractive index. For forbidden transition in the case of simple parabolic bands,

\[ \alpha = A(E) \left( \frac{hv}{E_g} \right)^{3/2} \]

where \( A(E) \) is a slowly varying function of energy.

In semiconductors where the minimum of the conduction band and the maximum of the valence band occur at different \( K \) values, optical transitions from the latter to the former require the participation of phonons in order to conserve momentum. This is because the electron wave vector will change hence phonons are either emitted or absorbed. The absorption coefficient for an allowed indirect transition is given by [38],

\[ \alpha = \frac{C \left( \frac{hv}{E_p - E_g} \right)^2}{\exp\left( \frac{E_p}{K_B T} \right) - 1} + \frac{C \left( \frac{hv}{E_g - E_p} \right)^2}{1 - \exp\left( - \frac{E_p}{K_B T} \right)} \]

where the first term represents the contribution of phonon absorption and must be taken to be zero if \( hv < E_g - E_p \), while the second term represents the contribution of phonon emission and is taken as zero for \( hv < E_g + E_p \). \( E_p \) is the phonon energy and \( C \) is a constant. Indirect transitions occur with a lower probability and give rise to an absorption edge that is less steep than for direct transitions. For forbidden indirect transitions,

\[ \alpha = C' \left( \frac{hv \pm E_p}{E_g} \right)^3 \]
where $C'$ is a slowly varying function of temperature and energy.

For heavily doped semiconductors, the absorption edge lies at much shorter wavelengths as compared to the intrinsic case. This effect is called the Moss-Burnstein Shift.

### 2.4 OPTICAL BAND GAP

The expression for the transmission coefficient, $T$ for a thin film of thickness $t$, absorption coefficient $\alpha$ and reflectivity $R$ is given by [38],

$$T = \frac{(1 - R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)}$$

(12)

In the equation, if $\alpha t$ is large, the second term in the denominator can be neglected. The simplified equation for the transmission coefficient takes the form,

$$T = \frac{(1 - R)^2 \exp(-\alpha t)}{1 - R^2}$$

(13)

OR

$$\alpha = \frac{1}{t} \ln \left[ \frac{(1 - R)^2}{T} \right]$$

(14)

If the thickness $t$, transmission coefficient $T$, and reflectivity $R$, are known for all wavelength range, the absorption coefficient $\alpha(\lambda)$ for any wavelength can be calculated using equation (14). The relationship between the absorption coefficient and the photon energy $h\nu$ is given by the equation (8), (9), (10) and (11). Thus the nature of the transition and band gap can be determined using these equations.
The transmittance $T$ and the reflectance $R$ at normal incidence at an interface between two media, with refractive indices $\eta_1$ and $\eta_2$ (which are complex) are given by [39, 40],

\[
R = \left[ \frac{\eta_1 - \eta_2}{\eta_1 + \eta_2} \right] \left[ \frac{\eta_1 - \eta_2}{\eta_1 + \eta_2} \right]^* \tag{15}
\]

\[
T = \left[ \frac{2\eta_1\eta_2}{\eta_1 + \eta_2} \right] \left[ \frac{2\eta_1\eta_2}{\eta_1 + \eta_2} \right]^* \tag{16}
\]

where the asterisk denotes a complex conjugate. $\left[ \frac{\eta_1 - \eta_2}{\eta_1 + \eta_2} \right]$ is called reflectivity $r$, and $\left[ \frac{2\eta_1\eta_2}{\eta_1 + \eta_2} \right]$ is called transmissivity $t'$. These equations are called Fresnel coefficients. At angles of incidence, $r$ and $t$ depends on the polarization of the incident wave. For a wave with electric vector in the plane of incidence,

\[
r_p = \frac{\eta_1\cos \theta_1 - \eta_2\cos \theta_2}{\eta_1 \cos \theta_2 + \eta_2 \cos \theta_1} \tag{17}
\]

\[
t'_p = \frac{2 \eta_1 \cos \theta_1}{\eta_1 \cos \theta_2 + \eta_2 \cos \theta_1} \tag{18}
\]

where $\theta_1$ and $\theta_2$ are the angles of incidence and refraction respectively. If $\eta_2$ is complex, $\theta_2$ will be complex and therefore, will not represent angle of refraction except for $\theta_2 = 0$. Only for this case will the Fresnel coefficients be defined.

For a wave with electric vector normal to a plane of incidence, we have

\[
r_s = \frac{\eta_1\cos \theta_1 - \eta_2\cos \theta_2}{\eta_1 \cos \theta_2 + \eta_2 \cos \theta_1} \tag{19}
\]

\[
t'_s = \frac{2 \eta_1 \cos \theta_1}{\eta_1 \cos \theta_2 + \eta_2 \cos \theta_1} \tag{20}
\]

The optical properties of a medium are characterized by complex parameters.
The real part generally gives an idea about dispersion while the imaginary part provides a measure of dissipation rate of the wave in the medium. Two complex parameters considered here are

(a) the refractive index given by

\[ \eta = \eta_r + i\kappa \]

where \( \eta_r \) is the ordinary real index and \( \kappa \) is the extinction coefficient.

(b) dielectric constant

\[ \varepsilon = \varepsilon_1 + i\varepsilon_2 \]

where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the real and imaginary dielectric constants.

The real and imaginary parts of the dielectric function are related to the optical constants by,

\[ \varepsilon_1 = \eta_r^2 - \kappa^2 \]

and

\[ \varepsilon_2 = 2\eta_r\kappa \]

In principle, \( \varepsilon_1 \) and \( \varepsilon_2 \) (or \( \eta_r \) and \( \kappa \)) can be obtained from any two independent spectrophotometric recordings by use of Fresnel's equations. The reflectivity \( R \), at any absorbing medium of indices (\( \eta_r, \kappa \)) in air for normal incidence is given by,

\[ R = \frac{(\eta_r - 1)^2 + \kappa^2}{(\eta_r + 1)^2 + \kappa^2} \quad \text{(21)} \]

and the transmittance \( T \), given by

\[ T = A (1 - R)(1 - R') \exp(-\alpha t) \quad \text{(22)} \]
when the interference and multiple reflections are neglected. $R$ and $R'$ are reflection coefficients at air-film and film-substrate interfaces respectively and $A$ is a constant. Parameters $\alpha$ and $t$ are the absorption coefficient and film thickness respectively. The absorption coefficient is related to the extinction coefficient by the expression

$$k = \frac{\alpha\lambda}{4\pi}$$  \hspace{1cm} (23)

where $\lambda$ is the wavelength of light.

2.6 THERMOELECTRIC POWER

One of the important methods for investigating electronic properties of solids is the measurement of thermoelectric power or seebeck coefficient as a function of temperature. A thermoelectric force (emf) is caused by a temperature gradient in a sample as a result of diffusion of carriers from warm to cold regions. When two ends A and B of a material are subjected to a temperature gradient under a condition in which no current is drawn, a thermoelectric force or a potential difference is developed between the two ends. This result is shown in figure 2.4.

For n-type materials, this effect arises as a result of the diffusion of electrons from the high temperature end to low temperature end, causing the build up of positive space charge near the high temperature end and negative space charge near the low temperature end. This sets up an electric field (or potential difference) to make the net current flow zero; hence the reference to the thermoelectric effect as a zero current coefficient. The thermoelectric power is defined by,

$$S = \frac{\Delta V}{\Delta T}$$ \hspace{1cm} (24)

where $\Delta V$ is the potential difference produced due to the temperature gradient $\Delta T$ between two points on a specimen.
Thermoelectric effect involves both charge carrier and energy transport. In metals the change of temperature does not change the concentration of electrons but brings about only a slight redistribution of their thermal velocities and it is obvious that large thermoelectromotive force cannot arise. In semiconductors, the change of temperature causes a change in both the concentration and the kinetic energy of mobile charge carriers. In an n-type semiconductor, in which the temperature at one end is higher than that at the other, the number of electrons diffusing from the hot end to the cold end is more than that in the opposite direction at the start.

Figure 2.4: Thermoelectric effect. Arrows show the direction of electron drift.
However, the difference in the electron flow between these two opposite directions gradually decreases to zero as an internal potential difference is set up between the two ends until the electron current due to diffusion process is equal to the reverse electron current caused by such a potential difference. Thus under a dynamic equilibrium, the net flow of electrons per unit time passing through any cross section of the semiconductor in both directions is zero. However, the velocities or the kinetic energies of electrons from the hot end are higher than those from the cold end through the same cross-section. This results in a continuous transfer of heat energy in the direction of the temperature gradient without involving actual charge transfer.

In general measurements of thermoelectric power provide useful information about the mechanisms of electrical transport. The polarity of the thermal emf indicates the types of the dominant carriers which take part in dominant electric conduction. The thermoelectric power \( S \) is negative if the majority charge carriers are electrons and the polarity of the thermal emf at the hot end is positive such that

\[
S = \frac{(dV/dx)}{(dT/dx)} < 0 \quad \text{(for n-type conduction)}
\]

and \( S \) is positive if the majority carriers are holes and the polarity of the thermal emf at the hot end is negative such that

\[
S = \frac{(dV/dx)}{(dT/dx)} > 0 \quad \text{(for p-type conduction)}
\]

The quantity \( S \) may be used to determine the position of the Fermi level, the concentration and mobility of carriers, the activation energy \( \Delta E \) of carrier generation which is important for the investigation of additional activation processes influencing the conductivity.

Specific relations for temperature dependence of \( S \) for both extrinsic and intrinsic conductivity may be obtained. To achieve this, let an n-type semiconductor form a junction with a metal whose work function \( \Phi_m \) is larger than that of the semiconductor, \( \Phi_c \). At equilibrium, the Fermi level must be the same in both materials and the electrons that flow from the metal to the semiconductor must absorb an amount of energy equal to \( (E_c - E_F) \) at the junction inorder to reach the edge of the conduction band of the semiconductor. The electrons which carry the
current in the semiconductor have a certain mean kinetic energy $\langle E \rangle$ so that the total energy change at the junction is $[ (E_e - E_F + \langle E \rangle )$]. The peltier coefficient $\Pi$ is defined by

$$\Pi = \frac{Q}{I} = ST$$  \hspace{1cm} (25)$$

where $Q$ is the heat evolved per second at the junction and $I$ is the current flowing through the specimen. $\Pi$ can also be interpreted as the mean energy transported per unit charge. It can therefore be written as,

$$\Pi = - \frac{[ (E_e - E_F + \langle E \rangle )]}{q}$$  \hspace{1cm} (26)$$

The mean kinetic energy $\langle E \rangle$ of the charge carriers depends on the precise form of the density of states distribution function and on the nature of the scattering processes. From equation (25) the thermoelectric power for n-type semiconductor can be written as

$$S = \frac{\Pi}{T} = - \frac{[ (E_e - E_F + \langle E \rangle )]}{qT}$$

$$= - \frac{(K_B / q) [(E_e - E_F) / K_B T + 5 / 2 + \gamma ]}{qT}$$  \hspace{1cm} (27)$$

where $\gamma$ is the temperature coefficient. Similarly for p-type semiconductors,

$$S = + \frac{(K_B / q) [(E_F - E_e) / K_B T + 5 / 2 + \gamma ]}{qT}$$  \hspace{1cm} (28)$$

In the case of predominantly lattice scattering, we have,

$$S = - \frac{(K_B / q) [(E_e - E_F) / K_B T + B ]}{qT}$$  \hspace{1cm} (29)$$

for n-type semiconductors and

$$S = + \frac{(K_B / q) [(E_F - E_e) / K_B T + B ]}{qT}$$  \hspace{1cm} (30)$$

for p-type semiconductors where $B$ is a constant which depends on the nature of the scattering process.
2.7 EVALUATION OF TRANSPARENT CONDUCTORS

Transparent conductors are evaluated from their optical transmission and conductivity both of which should be as large as possible. Haacke [41] defines a term $\Theta_{TC}$ called the figure of merit which is used to evaluate transparent conductors.

$$\Theta_{TC} = \frac{T^{10}}{R_s}$$  \hspace{1cm} (31)

where $T$ is the optical transmission and $R_s$ is the electrical sheet resistance. If reflection losses from the transparent surface are negligible, then $T$ can be written as,

$$T = \exp (-\alpha t)$$  \hspace{1cm} (32)

Defining sheet resistance as

$$R_s = \frac{1}{\sigma t}$$  \hspace{1cm} (33)

where $\alpha$ is the absorption coefficient in cm$^{-1}$, $t$ is the film thickness in cm and $\sigma$ is the conductivity.

$\Theta_{TC}$ can therefore be obtained as,

$$\Theta_{TC} = \sigma t \exp (-10\alpha t)$$  \hspace{1cm} (34)

Equation (34) correlates the figure of merit with the material parameter $\alpha$ and $\sigma$. If reflection losses cannot be neglected, equation (32) becomes,

$$T = (1 - R^2) \left[ \exp (\alpha t) - R^2 \exp (-\alpha t) \right]^{1/2}$$  \hspace{1cm} (35)

where $R$ is the reflectivity. Equation (34) then becomes

$$\Theta_{TC} = \sigma t \left[ (1 - R^2) \exp (\alpha t) - R^2 \exp (-\alpha t) \right]^{10}$$  \hspace{1cm} (36)

27
The above equation can be used to predict the transparent electrode properties of a material from the fundamental material parameters $\alpha$, $\sigma$ and $\eta$.

2.8 SOLAR CELL OPERATION

2.8.1 Introduction

Solar cell operates like a diode in which incident photons are absorbed and create electron hole pairs. The conversion of sunlight into electrical energy in a solar cell takes place in three processes i.e absorption of the sunlight in the semiconductor material; generation and separation of holes and electrons creating a voltage in the solar cell and then the transfer of these free charges to the outside application in form of electric current through electrical terminals.

2.8.2 Photoelectric effect

Photoelectric effect is the absorption of light in the semiconductor so as to create electron - hole pairs. The electron hole pairs created give excess carriers which is above the equilibrium concentration. The rate of generation is given by

$$G(\lambda, x) = \alpha(\lambda) N(0, \lambda) \exp(-\alpha(\lambda)x) \quad (37)$$

where $\alpha(\lambda)$ is the absorption coefficient for the wavelength $\lambda$ and $N(0, \lambda)$ is the number of incident photons per unit area per second at that wavelength at the surface. The carriers have a finite lifetime and recombine with each other after a characteristic lifetime $\tau$. The two carriers must be separated and transferred to external contacts of the cell in order to use the energy in the electron - hole pairs.

2.8.3 Separation and collection of carriers

When an n-type and p-type materials are brought in to contact, the electrons in the n-type material will diffuse in the p-type material due to statistical force giving rise to diffusion current.
The same process happens for the holes. In equilibrium, the donor ions in the n-type region near the interface will not be compensated by the electrons. Similarly, the acceptor ions in the p-type region near the interface will not be compensated by the holes. A dipole will therefore be created making the n-type positively charged with respect to the p-type region. The figure 2.5 shows this effect.

The electrostatic potential barrier resulting in an electric field will attract electrons from the p-type region towards the n-type region and holes from the n-type region to the p-type. The electrostatic built-in potential $V_D$ will adjust its value such that the statistical diffusion force acting on the electrons is exactly balanced by the electrical force. From figure 2.5, the electrostatic energy is higher at the p-side than at the n-side. However the total energy which is equal to the sum of the electrostatic and chemical energy, giving rise to the diffusion force is constant.

The electron current flowing from the n-type to the p-type region strongly depends on the barrier height. The n-type region forms an infinite electron source but only those electrons having enough energy will be able to diffuse over the built-in potential barrier $V_D$ and to recombine in the p-type region. Such an electron transport process is characterized by an exponential dependence on the barrier height typical for a Boltzmann distribution. This current referred to as the recombination current $I_r$, is given by

$$ I_r = I_o \exp\left(-\frac{qV_D}{K_BT}\right) = I_{g,d} \quad \text{(38)} $$

where $K_B$ is the Boltzmann constant, $T$ the absolute temperature and $I_o$ is the dark saturation current. This current is compensated by the dark generation current of electrons in the p-type region $I_{g,d}$. The current $I_{g,d}$ is independent of the barrier height and is determined by the availability of electrons on the p-side. These electrons are thermally generated. When the diode is illuminated, the electron concentration at the p-side increases.
Figure 2.5: Electron electrostatic energy1 and total electrochemical energy corresponding to the Fermi level 2 in un-illuminated diode.
If no external contact between n and p parts is made (open circuit), the current $I_{g,d}$ will strongly increase to the value $I_{g,l}$ (under light). To maintain a zero electron current, the recombination current will also increase, thus lowering the electrostatic built-in voltage by an amount $V_{oc}$ such that,

$$I_{g,d} + I_{g,l} = I_o \exp \left[-\frac{q (V_D - V_{oc})}{K_B T}\right] \quad \text{(39)}$$

Figure 2.6 shows this effect. The total electron energy is now higher in the n-type part than in the p-type by an amount $qV_{oc}$. When a voltmeter with infinite impedance is connected between A and B, it will measure an open circuit voltage equal to $V_{oc}$. In practice, $V_{oc}$ is considerably small and the situation illustrated by figure 2.6 holds. Combination of equation (38) and (39) gives

$$I_{g,l} = I_{g,d} \exp \left(\frac{qV_{oc}}{K_B T} - 1\right) \quad \text{(40)}$$

$$V_{oc} = K_B T / q \left[ \ln \left(\frac{I_{g,l}}{I_{g,d}}\right) + 1 \right] \quad \text{(41)}$$

The open circuit voltage depends in a logarithmic way on the relation between the light generated ($I_{g,l}$) and the dark generated ($I_{g,d}$) current.

The operation of a solar cell therefore can be modeled by a current source and a diode in parallel as shown in figure 2.7. The ideal I - V characteristics of such devices are given by [3],

$$I = I_s \{\exp \left[(qV / K_B T)\right] - 1\} - I_L \quad \text{(42)}$$

$$J_s = I_s / A = q n_i^2 \left[ 1 / N_A (D_n / \tau_n)^{1/2} + 1 / N_D (D_p / \tau_p)^{1/2} \right] \exp(-E_g / K_B T) \quad \text{(43)}$$

where

$I_s$ - saturation current, $I_L$ - strength of the constant current source due to incident light,

$A$ - the device area, $K_B$ - Boltzmann constant, $T$ - temperature, $q$ - electronic charge,
Figure 2.6: Electron electrostatic energy 1 and total energy 2 in an illuminated diode.
Figure 2.7: p-n junction solar cell irradiation and idealized equivalent circuit.
V - voltage, I - current, \( D_n, D_p \) - diffusion coefficients of electrons and holes respectively, 
\( \tau_n, \tau_p \) - lifetimes of electrons and holes, \( N_A, N_D \) - concentration of acceptor and donor impurities respectively and \( n_i \) - the intrinsic carrier density.

The equations (38) to (43) and the equivalent model in figure 2.7 are for ideal solar cell in which the recombination current obeys Boltzmann law. This is not the case in practical solar cells.

In order to obtain a better insight in the actual collection of the generated carriers, more details about the current mechanisms are necessary. For one dimensional case, the basic semiconductor device equations are,

(1) Current transport equations

\[
J_n = q \mu_n nE + qD_n \frac{dn}{dx} \quad \text{(44)}
\]

\[
J_p = q \mu_p pE - qD_p \frac{dp}{dx} \quad \text{(45)}
\]

(2) Continuity equations

\[
\frac{\partial n}{\partial t} = G - U + \frac{1}{q} \frac{dn}{dx} \quad \text{(46)}
\]

\[
\frac{\partial p}{\partial t} = G - U - \frac{1}{q} \frac{dp}{dx} \quad \text{(47)}
\]

(3) Poisson's equations

\[
\frac{\partial E}{\partial x} = q \epsilon \left[ N(x) + p - n \right] \quad \text{(48)}
\]

where \( J_n \) and \( J_p \) are electron and hole current densities respectively, \( E \) is the electrostatic field, \( \mu \) is the mobility, \( D \) is the diffusion coefficient, \( q \) is the electronic charge and \( N(x) \) is the purity density distribution. \( G \) is the total generation rate due to light for all wavelength. \( U \) is the net
thermal recombination generation rate, modeled by Schottky - Read - Hall in terms of trapping level located in the band gap and is expressed as,

\[
U = p_n - n_i^2 / \tau_{po} ( n + n_1 ) + \tau_{no} ( p + p_1 )
\]

where \( n_i \) is the intrinsic carrier density, \( \tau_{po} \) and \( \tau_{no} \) are minority hole and electron lifetimes respectively, \( n_1 \) and \( p_1 \) are the electron and hole densities which exist if the Fermi level were located at the trapping level, \( n \) and \( p \) are the electrons and holes respectively.

2.8.4 The metal insulator semiconductor (MIS) and the semiconductor insulator semiconductor (SIS) solar cells

These cells present very promising possibilities in getting away with the cells having p - n junctions and replacing them by deposited metal - insulator junctions [42]. This contact has been used for many years to make other types of semiconductor devices. MIS cells are the outgrowth of work on thick insulator MIS field effects. It was found that if the insulator was made sufficiently thin ( < 60Å ) then quantum mechanical tunneling currents could flow through the insulator and couple to the induced p - n junction. It was also established that very thin insulator brings non equilibrium mode of operation which creates a potential difference. The current transport through the thin interfacial layer by tunneling provides an ohmic contact, thus the properties of a p - n junction could be achieved without forming the junction by a conventional conductivity type.

It was later discovered that devices consisting of conducting oxides applied to silicon could also achieve good photovoltaic conversion efficiencies [43, 44]. These devices which had been previously studied extensively as photosensors, also relied on the presence of a thin interfacial layer. Their operation is similar to MIS solar cells [45], except that the metal is replaced by a transparent conducting semiconductor. These conductors are mostly oxides ( SnO₂ , In₂O₃ ) or mixtures of these. The oxides act as transparent conducting metals but there is a big contrast between the MIS and SIS configuration. The MIS mode require a thin (~ 50 Å) metal
film so as to transmit light transmission whereas conducting oxide being transparent can be several thousand Å. The transparent oxides must be degenerately doped so as to conduct. The fact that the transparent conducting semiconductor permits the transmission of light and are effectively metals means that the requirement of the collection grid can be greatly reduced. The refractive index of these materials make them suitable to be used as partial anti-reflection coatings.

The figure 2.8 shows simple energy band diagram for the SIS system. The energy band gaps and the barrier heights have been chosen to reflect the (n-type) ITO - SiO₂ - (p-type) Is. This is the most commonly studied SIS structure. The key parameters in this diagram are the potential barrier heights \( \phi_{osi} \) and \( \phi_{si} \). The energy difference between the silicon semiconductor and silicon dioxide insulator conduction band edges (\( E_{ci} \) and \( E_{cs} \)) is \( \phi_{si} = 3.2 \) eV. For (n-type) ITO - SiO₂, \( \phi_{osi} = 3.3 \) eV. Obviously \( \phi_{osi} \) control the degree of inversion of the p-type semiconductor. To invert the surface of a p-type semiconductor to n-type requires \( \phi_{osi} \) to be low in value. A high value will accumulate the surface, i.e more p-type. The demarcation point occurs at approximately 3.6 eV. If \( \phi_{osi} \) is low, then the dominant tunnel current flow near zero bias is by minority carrier (conduction) band. This is called minority carrier tunnel SIS diode. On the other hand, if \( \phi_{osi} \) is high, the surface is accumulated and the dominant current is by majority carriers and is called a majority carrier tunnel SIS diode. The tin oxide on (n-type) silicon forms a minority carrier diode and indium oxide on (p-type) silicon is also a minority carrier diode. Minority carrier diodes are very useful in photovoltaic conversion. The I - V characteristics of such diodes can obey the ideal Schottky diode equation over a certain bias range.

2.8.5 Effect of interfacial layer thickness

It has been observed earlier that one of the key parameters which control the efficiency of the SIS solar cell is the thickness of the interfacial layer. Therefore it is of interest to consider the effect of decreasing interfacial layer thickness on the performance of SIS diode. The appropriate range of thickness is 10 - 30 Å, the upper limit being the value at which the ITO - Si diode would
$\phi_{osi} = 3.3$ eV

$E_F$, $0.1$ eV

$E_{gms} = 3.6$ eV

$E_{vos}$

Interfacial states

$E_{vi}$

Interfacial region

$E_{ci}$

$\phi_{m} = 3.2$ eV

$E_{gs} = 1.12$ eV

neutral region

depletion region

Figure 2.8: Semiconductor Insulator Semiconductor Cell (SIS) [45].
revert to equilibrium mode of operation and the lower limit is the value beyond which Schottky diode behaviour sets in. Figure 2.9 shows the dependence of diode performance on the insulator thickness. The figure shows the conversion efficiency as a function of insulator thickness for two typical values of substrate resistivity. For an interfacial layer thickness greater than \(20\,\text{Å}\), the efficiency is very low but rises rapidly with decreasing thickness and then stabilizes at about \(15\,\text{Å}\). In the region from \(15 - 20\,\text{Å}\), the decrease in efficiency can be attributed to increase in the effective resistance from: the exponential change in tunnel current with thickness and the change in I-V characteristics owing to the transition from the semiconductor - current limited to the tunnel - current limited mode. This conclusion is supported by the calculations for \(J_{sc}\) and fill factor (FF), which is illustrated in figure 2.10. The stabilization of the efficiency below about \(15\,\text{Å}\) is explained by the fact that at that point, tunneling occurs at a sufficiently high rate such that the effective resistance via this process becomes insignificant and all possible current from the semiconductor is extracted [45].

2.9 CELL CHARACTERIZATION

If the back and front contacts of a cell are connected to one another, a current flows from the front to the back contact without any voltage. This is the maximum current across the diode and is called the short circuit current. The total diode current under illumination is given by equation (42) which can be expressed in the form of current density as,

\[
J = J_s [ \exp \left( \frac{q V}{K_B T} \right) - 1 ] - J_L \quad \text{--------------------- (50)}
\]

Voltage generated in an open circuit cell is maximum while the current is zero. If \(J\) is set equal to zero in equation (50), the open circuit voltage is given by

\[
V_{oc} = \left( \frac{K_B T}{q} \right) \ln \left[ J_L / J_s + 1 \right] \quad \text{--------------------- (51)}
\]
Figure 2.9: Computed effect of insulator thickness on conversion efficiency of an ITO - SiO₂ -(p-type) Si tunnel diode with carrier concentration as a parameter [45].

- $N_{ss}$ - surface density of surface states per unit energy;
- $Q_{i}$ - surface charge density;
- $N_{A}$ - carrier concentration.
Figure 2.10: Variation of short circuit density $J_{sc}$, open circuit voltage $V_{oc}$ and fill factor $FF$ as a function of insulator thickness for an ITO - SiO$_2$ - (p-type) Si tunnel diode with carrier concentration as a parameter [45].
The open circuit voltage source can supply a current if an external load is connected across it. To find voltage that will produce maximum power, the power output of the device is computed.

\[
P = JV = \{ J_s [ \exp ( qV / K_B T ) - 1 ] - J_L \} V \quad \text{(52)}
\]

Taking the derivative of equation (52) and setting the result equal to zero yields an implicit equation for the voltage that maximizes the power, \( V_m \).

\[
\exp [ qV_m / K_B T ][ 1 + qV_m / K_B T ] = 1 + J_L / J_s = \exp ( qV_{oc} / K_B T ) \quad \text{(53)}
\]

Combining expressions (53) and (42), current that gives maximum power, \( J_m \) is,

\[
J_m = \frac{[qV_m / K_B T] J_L}{1 + J_s / J_L} \quad \text{------------------- (54)}
\]

Therefore the maximum power is given by

\[
P_m = J_m V_m = \frac{[qV_m / K_B T] V_m J_L}{1 + J_s / J_L} \quad \text{------------------- (55)}
\]

The solar cell efficiency is given by

\[
\eta = ( J_m V_m / P_{in} ) \times 100 \quad \text{------------------- (56)}
\]

where \( P_{in} \) is the input light power. \( J_{sc} \) and \( V_{oc} \) are called the short circuit current density and open circuit voltage respectively. Fill factor (FF) is defined as a ratio of the maximum power output to the product of \( J_{sc} \) and \( V_{oc} \).

\[
FF = P_m / V_{oc} J_{sc} \quad \text{------------------- (57)}
\]
Fill factor is useful as a measure of the realizable power from the I - V curve. Typical values for commercial cells lie in the range of 0.7 to 0.8.
CHAPTER THREE.

EXPERIMENTAL PROCEDURES.

3.0 INTRODUCTION.

Spray pyrolysis technique has been used to deposit undoped Zinc Oxide and Fluorine doped Zinc Oxide thin films. The technique involves spraying aqueous solution containing soluble salts of the constituent atoms of the desired compound on a substrate at high temperatures. The sprayed droplet reaching the hot substrate surface undergoes pyrolytic (endothermic) decomposition and forms a single crystallite or a cluster of crystallites of the product. Other volatile by-products and the excess solvent escape in the vapour phase. The hot substrate provides the energy for the thermal decomposition and subsequent recombination of the constituent species followed by sintering and recrystallization of the clusters of crystallites results to a coherent film.

This technique has been used successfully in glass works, metal coatings, semiconductor device manufacturing etc. It is a major process employed in chemical vapour deposition (CVD) of metal and alloy thin films. This is done by thermal decomposition or pyrolysis of organometallic compounds, hydrides, metal hydrides generally at low temperatures [46].

3.1 THE EXPERIMENTAL SET UP.

The spray pyrolysis apparatus was designed for the experiment. The spray made of glass has two inlets, one for the solution and the other is for the carrier gas. It has a single outlet which is very fine capillary. The experimental set up is shown in figure 3.1. Nitrogen was used as the carrier gas. Corning glass slides (75 x 25 mm) and 0.96 mm thick were thoroughly cleaned by using detergent and then acetone to remove any impurities (grease-particles). The slides were then placed on a hot plate whose temperature was slowly raised and controlled by a variac. The temperature monitoring was done by Iron / Copper-Nickel thermocouple and a multimeter [47].

Trial sprayings were carried out to determine the best gas pressure, spray height and the temperature that would give the best film. After obtaining a suitable gas pressure, height
Figure 3.1: Experimental set up for spray pyrolysis technique.
and temperature, the solution was sprayed on the glass substrate for a few seconds and then spraying stopped to allow the temperature of the substrate to rise back to the optimum value. Spraying was repeated until a thin film was formed on the glass substrate. The spray was moved over the slides slowly while spraying in order to obtain a uniform film.

3.2 FILM PREPARATION.

In the preparation of the films, the spraying mixture consisted of 0.1M Zinc acetate solution in a mixture of Isopropyl alcohol and water (volume ratio 3 : 1). For doping a few atomic percent of Fluorine in the form of Ammonium fluoride was added to the solution. Partial precipitation of ZnO was observed in the solution. This was reduced by the addition of a few drops of acetic acid in the solution. The solution was then sprayed on to a hot glass substrate held at a specific temperature. The temperature range for this experiment was 400 to 560°C. The substrate temperature fluctuation was maintained to within ± 5°C. The carrier gas used was whitespot Nitrogen. Films of Zinc Oxide and Fluorine doped Zinc Oxide were formed on the substrate. The films were cooled to room temperature after deposition to avoid annealing effects which could change some properties of the films. The transmission of light through the films was measured by UV spectrophotometer. The sheet resistance of the films was measured by Intelligent digital multimeter.

3.3 ANNEALING STUDIES.

Annealing studies were carried out on the undoped and doped films of ZnO deposited by spray pyrolysis in vacuum and air ambients. The films were placed in a vacuum of about $2 \times 10^{-5}$ Torr. and then heated using a radiant heater up to 130°C. The films were then annealed for three hours. Air at atmospheric pressure was the ambient for the air - annealed samples. The sheet resistance of the films was measured during the heating and cooling cycles. The optical and electrical properties of as - deposited and annealed films were then studied and results given in chapter four.
3.4 DETERMINATION OF ENERGY GAP.

A ratio recording technique [48] was used to determine the band gap of the films. In this technique the transmittance of a thicker film relative to a thinner film was measured. The net result is equivalent to measuring the transmission of a hypothetical film of thickness equal to the difference of the thickness of the two films without the reflection losses. If $T_{1-2}$ is the ratio of transmission and $\Delta t$ is the thickness difference then,

$$ T_{1-2} = \exp (-\alpha \Delta t) $$  

where $\alpha$ is the absorption coefficient.

From $T_{1-2}$, $\alpha \Delta t$ was computed from the equation (58). For direct transitions (eq. 8), a plot of $(h\nu\alpha \Delta t)^2$ against $h\nu$, where $h\nu$ is the incident energy gives a straight line which on extrapolation cuts the energy axis at the band gap level.

3.5 DETERMINATION OF FILM THICKNESS.

The thickness of the film was determined by using a UV spectrophotometer. By using a specular reflection attachment shown in figure 3.2, to deflect the spectrophotometer beam up to the reflecting surface and then back again into the instrument while the wavelength is varied. For a fixed thickness $t$, the reflected intensity will vary cyclonically. For various extrema, the thickness was calculated from [49],

$$ t = \frac{M \lambda_1 \lambda_2}{2 \eta (\lambda_2 - \lambda_1)} \text{ } (59) $$

where $M$ is the number of oscillations between the two extrema occurring $\lambda_1$ and $\lambda_2$. The value $\eta$ is taken to be the refractive index of bulk Zinc oxide. This method is attractive because $t$ is determined precisely in the region of the film where transmission is measured.
Figure 3.2: The experimental set up for measuring film thickness.
3.6 THERMOELECTRIC POWER.

Thermoelectric power measurements were carried out on the annealed samples. They were placed in drilled insulators (corks) of appropriate sizes. The insulators were employed to facilitate the creation of a temperature gradient between the two ends of the samples.

The high temperature investigations involved the heating of one end of the samples while the other end was left at room temperature. Two Copper/Nickel thermocouples were fixed at the two ends to monitor the temperatures. The figure 3.3 shows the experimental set up. The voltage drop (ΔV) corresponding to ΔT was measured on a digital multimeter. The expression for thermopower is given in equation (24). The mean value of the temperatures at the two ends of the samples were used as the ambient temperature.

Errors may arise in this experiment particularly in determining the temperature gradient. This was avoided by using calibrated thermocouples. An emf appearing when ΔT is zero is attributed to an uneven distribution of impurities in the film.

3.7 CELL FABRICATION.

In this section, a 1.35 Ω cm p-type silicon wafer was cleaned in acetone and then etched using 49% Hydrofluoric acid (HF). Etching was done to remove any native oxide on the silicon wafer. After about five minutes, the wafer was rinsed in distilled water and an oxide layer was grown on the silicon wafer by placing it in concentrated Nitric acid at about 60°C for a few seconds. The wafer was again cleaned in distilled water. The procedure is similar to that used by Singh et al [50]. The substrate was then heated on a hot plate up to a temperature of 480°C and Fluorine doped ZnO film was deposited on it by spray pyrolysis technique.
Figure 3.3: Schematic diagram for thermoelectric power measurements.
Annealing in a vacuum of $2 \times 10^{-5}$ Torr. and a temperature of $130^\circ$ C was done on the cell for about three hours. Aluminium back contact was applied to the un-polished side of the cell by using the vacuum coating unit.

Aluminium grid was applied to the cell by placing a grid mask on top of the side on which the doped ZnO layer had been grown and aluminium deposited using the vacuum coating unit.

3.8 DETERMINATION OF THE PARAMETERS OF THE CELL.

A solar cell can be represented by an equivalent circuit shown in figure 2.7 (chapter two). The model is an idealized circuit of a solar cell where the series resistance is zero and shunt resistance is infinity. Series resistance is due to the resistivity of the bulk materials, the resistance of the depletion region and the resistance of the contacts. Shunt resistance ($R_{sh}$) results from junction defects which determine leakage currents across junction. An equivalent circuit of a practical solar cell is shown in figure 3.4.

The set up for the measurements of the I - V characteristics of the cell is shown in figure 3.5. The I - V characteristics were measured under direct sunlight of intensity 80mW/cm$^2$. In the laboratory, a white light source placed at a distance of 25 cm was used to give the same results. The voltage was supplied by a variable power supply that works in opposition with a battery. The combination of a battery and a power supply simulates a variable load to the cell. The voltage and the current were measured and recorded. A typical I - V curve is shown in figure 3.6. The dark I - V characteristics of the cell were determined in the dark.

Several parameters can be derived from figure 3.6. Light generated current ($I_L$) equals the short circuit current which can be determined on the I - V curve. When the series resistance ($R_{sc}$) and the parallel resistance ($R_p$) are both high, there will be a leakage through $R_p$ and $I_S$ will be smaller than $I_L$, but this is negligible in good solar cells. The open circuit voltage ($V_{oc}$) can also be determined from the I - V curve.
Figure 3.4: Equivalent circuit of a practical solar cell.
Figure 3.5: Set up for the I-V measurements.
Figure 3.6: Typical $J - V$ characteristic of a solar cell.
3.9 DETERMINATION OF SERIES RESISTANCE OF THE CELL.

The series resistance of the cell was obtained by illuminating the cell at two different intensities and plotting their I - V characteristics. From figure 3.7, the series resistance $R_{se}$, is

$$R_{se} = \frac{V_1 - V_2}{I_2 - I_1}$$

On the I - V curve, the maximum power point can be determined. This is the point where the product IV is maximum. This can be done easily when the curve is drawn on a paper that contains lines of constant IV product. After getting these parameters, the efficiency of the solar cell and the Fill Factor were computed using equations (56) and (57) in chapter two.
Figure 3.7: Measurement of series resistance $R_{se}$ of a solar cell. I-V characteristics at two different intensities.
CHAPTER FOUR
RESULTS AND DISCUSSION.

4.0 INTRODUCTION

The electrical and optical properties of Fluorine doped Zinc oxide films deposited by spray pyrolysis technique are discussed in this chapter. The chapter also discusses the annealing effects on the optical and electrical properties. The optimum conditions obtained in the preliminary results are outlined below. The spray height was established to be 28 cm, the spray rate was 12 cm³/min., the carrier gas pressure was 8 lbf/in² (approximately $5.6 \times 10^4$ N/m²) and the substrate temperature was $480^0$ C. These conditions produced the best films of Fluorine - doped Zinc oxide. It was established that for low spray height, the substrate cracked due to rapid cooling, while for higher height, the films had very high sheet resistance and a lot of the solution was wasted. High spray rate gave poor optical quality of the films since white spots could be observed on the surface of the substrate. This was due to big droplets which could not decompose easily on reaching the glass substrate surface and hence leaves white precipitate. Low spray rate produced films with very high sheet resistance. This could be due to annealing in air since it took longer time to grow the films. The annealing in air could be due to trapping of oxygen in the grain boundaries which inhibits the free movement of the charge carriers hence an increase in the resistivity of sheet resistance.

4.1 ELECTRICAL PROPERTIES.

In this section, the electrical properties of the ZnO films deposited by spray pyrolysis technique are presented. The sheet resistance of the films grown at different temperatures is shown in table 4.1. The results are graphically shown in figure 4.1 and it shows a drop in the sheet resistance as the temperature rises. The drop in sheet resistance reaches a minimum at a temperature of $480^0$ C. This was obtained by free hand drawing as shown in figure 4.1. The sheet resistance at this temperature was found to be $197K\Omega$. However, computer fit gave the temperature to be approximately $485^0$ C which is within the experimental error of $\pm 5^0$ C. Beyond this temperature, the sheet resistance began to rise to about $500K\Omega$ at a temperature of $560^0$ C. The high sheet resistance at temperatures below $480^0$ C could be due to incomplete
reaction leaving some impurities at the grain boundaries. The high resistance at higher substrate temperatures could be attributed to cracked films and most of the solution evaporated resulting to more time for deposition which could lead to annealing effects. Zinc oxide films deposited at optimum conditions gave sheet resistance in the range of 197 to 240KΩ.

Table 4.1: Sheet resistance for ZnO films deposited at various temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Sheet resistance (KΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>410</td>
<td>810</td>
</tr>
<tr>
<td>440</td>
<td>622</td>
</tr>
<tr>
<td>450</td>
<td>396</td>
</tr>
<tr>
<td>460</td>
<td>310</td>
</tr>
<tr>
<td>480</td>
<td>197</td>
</tr>
<tr>
<td>500</td>
<td>254</td>
</tr>
<tr>
<td>520</td>
<td>308</td>
</tr>
<tr>
<td>540</td>
<td>424</td>
</tr>
<tr>
<td>560</td>
<td>500</td>
</tr>
</tbody>
</table>

The optimum temperature which gave the least sheet resistance was then used in deposition of F: ZnO films. The doping was done by adding a few atomic percent of Fluorine in the spray solution in the form of Ammonium fluoride. The results obtained for doping are presented in table 4.2. It was observed that the sheet resistance decreased as the doping concentration was increased from 0 to 1.5% as shown in figure 4.2. Fluorine doping gives rise to electrons since the impurities are ionized. The ionized fluorine causes scattering which is an unavoidable result of doping hence the electrons become mobile and move freely. The free electrons results to a decrease of resistivity hence the low sheet resistance. The decrease in resistivity also results in the increase of conductivity which is the main objective of doping.
Figure 4.1: Variation of sheet resistance with temperature for undoped ZnO films.
It is observed that doping with fluorine beyond 1.5% results to an increase of sheet resistance. The excess ions produced in this case hinders the carrier mobility. Excess doping also leads to the formation of different absorbing complexes which diminish the conductivity and transmittance. This could be observed on the substrate because at a doping beyond 1.5%, the glass substrate became cloudy with some brownish colour forming on it. This brownish colour could be the excess fluorine left after maximum doping level was obtained.

Table 4.2: Sheet resistance of undoped and Fluorine doped ZnO films (as - deposited).

<table>
<thead>
<tr>
<th>Doping concentration (%)</th>
<th>Sheet resistance (KΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>197.00</td>
</tr>
<tr>
<td>0.80</td>
<td>21.20</td>
</tr>
<tr>
<td>1.50</td>
<td>16.00</td>
</tr>
<tr>
<td>2.00</td>
<td>18.40</td>
</tr>
<tr>
<td>2.50</td>
<td>20.00</td>
</tr>
<tr>
<td>3.00</td>
<td>30.10</td>
</tr>
<tr>
<td>4.00</td>
<td>38.00</td>
</tr>
</tbody>
</table>

4.1.1 Annealing studies.

The annealing studies were carried out on Zinc oxide films which were undoped and doped. The doped films on which annealing was carried on, were of 0.8, 1.5, 2.5, 3.0 and 4.0 atomic percent of fluorine. The effects of annealing in air and vacuum was observed to be qualitatively similar for all the samples. The electrical sheet resistance decreased on annealing in vacuum and increased on annealing in air. This is consistent with previous reports for pure and antimony doped tin oxide film [50], pure and indium doped zinc oxide films [18].
Figure 4.2: Variation of sheet resistance with Fluorine doping concentration (as-deposited).
The fluorine content in the films determined the magnitudes of the changes in the sheet resistance of the films. The greatest change in sheet resistance was observed in pure zinc oxide and films containing 1.5% of fluorine exhibited the least change in the sheet resistance. The sheet resistance of the films after annealing in vacuum are shown in table 4.3.

**Table 4.3: Sheet resistance of undoped and Fluorine doped ZnO films as - deposited and annealed in vacuum for three hours at 130° C.**

<table>
<thead>
<tr>
<th>Doping conc. (%)</th>
<th>Sheet resistance (KΩ)</th>
<th>Vacuum annealed (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>197.00</td>
<td>1860.00</td>
</tr>
<tr>
<td>0.80</td>
<td>21.20</td>
<td>700.00</td>
</tr>
<tr>
<td>1.50</td>
<td>16.00</td>
<td>272.00</td>
</tr>
<tr>
<td>2.00</td>
<td>18.40</td>
<td>364.40</td>
</tr>
<tr>
<td>2.50</td>
<td>20.00</td>
<td>516.70</td>
</tr>
<tr>
<td>3.00</td>
<td>30.10</td>
<td>568.50</td>
</tr>
<tr>
<td>4.00</td>
<td>38.00</td>
<td>921.00</td>
</tr>
</tbody>
</table>

Annealing was carried out on undoped zinc oxide film in vacuum and air. Figure 4.3 shows the behaviour in the sheet resistance of the sample in both the vacuum and air ambients. The initial sheet resistance of the film was 197KΩ. The film was first heated in vacuum (2 × 10⁻⁵ Torr.) to a temperature of 130° C. The sheet resistance reduced to 6.13KΩ via curve (a). The sample was then cooled in vacuum and the sheet resistance rose to 20.70KΩ via curve (b). The sample was then heated in air at an atmospheric pressure which resulted in to an increase of sheet resistance to 60KΩ via curve (c). When the film was cooled in air, the sheet resistance increased to about 1.8MΩ via curve (d).

The above results show that the sheet resistance increases when annealed in air and decreases when annealed in vacuum. This rules out the possibility of significant structural changes on annealing. It is because the films were deposited at higher temperatures of 480° C while annealing was done at
Figure 4.3: Variation of sheet resistance with temperature on annealing in vacuum and air of ZnO film (undoped).

(a) Annealing in vacuum  (b) cooling in vacuum  (c) annealing in air  (d) cooling in air.
a temperature of 130°C. It was also observed that sheet resistance decreases when annealed in vacuum and increases when annealed in air. The data is given in appendix D.

The changes in resistivity of the films can be explained on the basis of chemisorption and desorption of oxygen at the grain boundaries of the polycrystalline zinc oxide films. Chemisorption of oxygen on zinc oxide surfaces have been studied by several workers [51, 52, 53] and is known to give rise to surface acceptor states. In the spray deposited ZnO films, the highly disordered intergranular regions provide sites for the chemisorption of oxygen on annealing in air. The chemisorbed oxygen at the grain boundaries is expected in as - deposited films since deposition was carried out in air at high temperatures. The chemisorbed oxygen increases the height of grain boundary which reduces the free movement of the charge carriers hence the sheet resistance becomes high.

In contrast, annealing in vacuum of the as - deposited film leads to desorption of oxygen from the grain boundaries. This in effect reduces the height of the grain boundary and as a result attribute to the creation or annihilation of oxygen acceptor states at the grain boundaries which act as traps for electrons. Desorption in effect increases the carrier mobility of the charges.

Figure 4.4 shows the variation of natural logarithm of the sheet resistance with the inverse of temperature for vacuum - annealed ZnO films doped with various concentrations of fluorine. The variation as observed in the figure gives a typical behaviour of a semiconductor. The variation of the resistivity is exponential i.e \( \rho = \rho_0 \exp \left( \frac{E}{K_B T} \right) \) where \( \rho_0 \) is the initial resistivity, \( E \) is the thermal energy and \( K_B \) is the Boltzmann constant. The activation energies obtained from figure 4.4 range between 0.47 - 0.65 eV. This is attributed to trap states due to chemisorption of oxygen at the grain boundaries of ZnO films. The activation energies obtained are within the experimental range [54].

4.1.2 Thermoelectric power.

Figure 4.5 shows the dependence of thermoelectric power with the inverse temperature. Thermoelectric power measurements was carried out on three doped films with 1.5, 2.0 and 4.0 atomic percent of fluorine. The thermoelectric power data is shown in appendix A1, A2 and A3. The figure 4.5 shows that the charge carriers of the films were of negative sign. This indicates that the conductivity was due to electrons ( n-type ). In the figure, the temperature means the ambient
Figure 4.4: Variation of $\ln R_s$ with $1000 / T$ of undoped and fluorine doped ZnO films.

(1) Undoped  (2) 3.0% doped  (3) 2.0% doped  (4) 1.5% doped.
Figure 4.5: Dependence of thermoelectric power with inverse temperature for differently doped ZnO films.
(a) 1.5% doped (b) 2.0% doped (c) 4.0% doped.
temperature of the films which is the mean of the temperatures at the two ends. The theoretical significance of measuring thermopower (S) is that on the assumption of the validity of the band theory, it gives a measure of the difference in energy between the Fermi level $E_F$ of the semiconductor and the conduction band for negative carriers. Thermopower measures the tendency of the free carriers to travel from the hot to the cold junction which gives rise to a temperature gradient in the film.

The negative thermopower values obtained is an indication that the conduction process involved in this case is n-type with electrons as the majority carriers. Fluorine doped zinc oxide film is therefore an n-type material with electrons as the majority carriers. Observed n-type conductance may be due to trapping effects, which is due to doping.

4.2 OPTICAL PROPERTIES.

In this section, the optical properties of undoped and Fluorine doped zinc oxide films are discussed. The transmission spectra for the undoped and doped ZnO film are shown in figure 4.6a. The spectra for doped films with different fluorine concentration is expressed in figure 4.6b. It is observed from the figure that there is a shift in the absorption edge towards the higher energy side. The doping also increases the transmission of the films. The shift in absorption edge towards the higher energy side on doping can be attributed to the Moss-Burnstein effect which occur as a result of filling up of low energy levels by the conduction electrons. The same results have been reported for antimony doped tin oxide films [55] deposited by spray pyrolysis technique.

The transmission spectra for as-deposited film and annealed film is shown in figure 4.7. It is observed that the transmission spectrum for vacuum annealed film is higher compared to the as-deposited film. The absorption edge also shifts to higher energy for the annealed ZnO films. The figure 4.8 shows transmission spectra for vacuum annealed films with different sheet resistances. The spectrum of the film with the least sheet resistance showed the highest transmission and the absorption shifted to the lower wavelength. Doping and annealing increases the transmission of the ZnO films. Beyond maximum doping, the ions form different absorbing complexes which diminish the transmittance [56]. The onset of infrared reflectance and high solar transmittance depends on the carrier concentration, hence highly
Figure 2.7: Transmission spectra for as-deposited and annealed film

(a) annealed (sheet resistance, 6.13kΩ)
(b) as-deposited (sheet resistance, 197kΩ)
Figure 4.6a: Transmission spectra for undoped and doped film.
(a) Undoped (sheet resistance, 205kΩ)
(b) 0.2% doped (sheet resistance, 21.2kΩ)
Figure 4.6b: Transmission spectra for different doping concentration.

(a) 1.5%  (b) 3.0%  (c) 2.0%
Transmission spectra for annealed films with different sheet resistance.

- Sheet resistance 272Ω (a)
- Sheet resistance 364Ω (b)
- Sheet resistance 516.7Ω (c)
doped films gave transmittance of about 82%. This transmittance was achieved by a doping level of 1.5% of fluorine after annealing.

The thickness $t$ of the films was calculated using equation (59) and the absorption coefficient $\alpha$, was computed using the transmission data and equation (14). The table 4.4 shows the absorption coefficient with corresponding photon energy. The dependence of absorption coefficient on the photon energy is shown in figure 4.9. It is observed that the absorption coefficient decreases with increases wavelength (decreasing photon energy). Ultraviolet rejection is of importance in the solar cell operation. Heavy doping shifts the absorption to smaller wavelengths, and the ultraviolet absorption becomes insignificant. As the visible region is approached, the absorption coefficient becomes smaller which allows for the visible light to be transmitted by the doped ZnO films hence increasing the performance of the films as a window material for solar cell application.

<table>
<thead>
<tr>
<th>Transmittance (T)</th>
<th>Wavelength $\lambda$ (µm)</th>
<th>$v = \frac{c}{\lambda}$ ($\times 10^{14}$) Hz</th>
<th>$h\nu$ (eV)</th>
<th>Absorption coefficient, $\alpha$ ($\times 10^5$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.067</td>
<td>0.3829</td>
<td>7.8349</td>
<td>3.246</td>
<td>2.04</td>
</tr>
<tr>
<td>0.100</td>
<td>0.3871</td>
<td>7.7499</td>
<td>3.210</td>
<td>1.74</td>
</tr>
<tr>
<td>0.200</td>
<td>0.3886</td>
<td>7.7200</td>
<td>3.197</td>
<td>1.31</td>
</tr>
<tr>
<td>0.300</td>
<td>0.3900</td>
<td>7.6923</td>
<td>3.186</td>
<td>1.04</td>
</tr>
<tr>
<td>0.400</td>
<td>0.3914</td>
<td>7.6648</td>
<td>3.174</td>
<td>0.853</td>
</tr>
<tr>
<td>0.500</td>
<td>0.3943</td>
<td>7.6084</td>
<td>3.151</td>
<td>0.702</td>
</tr>
<tr>
<td>0.600</td>
<td>0.3957</td>
<td>7.5815</td>
<td>3.140</td>
<td>0.569</td>
</tr>
<tr>
<td>0.700</td>
<td>0.3986</td>
<td>7.5263</td>
<td>3.117</td>
<td>0.451</td>
</tr>
<tr>
<td>0.800</td>
<td>0.4043</td>
<td>7.4202</td>
<td>3.073</td>
<td>0.338</td>
</tr>
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</table>
Figure 4.9: Dependence of absorption coefficient on photon energy.
The band gap of fluorine doped zinc oxide films was determined by considering two films of different thicknesses. The films were deposited at optimum conditions but for different duration of coating. The transmission spectrum of a thicker film relative to a thinner film of zinc oxide is shown in figure 4.10. The values of transmittance was computed and given in table 4.5. From the table, \((\alpha\Delta t \ h\nu)^2\) was calculated and a graph of \((\alpha\Delta t \ h\nu)^2\) verses \(h\nu\) was drawn and given in figure 4.11. Direct band gap of ZnO was obtained by extrapolation of the plot to cut the energy axis. The band gap was found to be 3.24 eV. This is similar to that reported by Aranovich et al [19], Zhi - Zheng et al [57].

Table 4.5: Values of transmittance, wavelength, photon energy and \((\alpha\Delta th\nu)^2\).

<table>
<thead>
<tr>
<th>T</th>
<th>(\lambda) ((\mu\text{m}))</th>
<th>(\nu = c/\lambda \times 10^{14}\ \text{Hz})</th>
<th>(\alpha\Delta t = -\ln T)</th>
<th>(h\nu) (eV)</th>
<th>((\alpha\Delta th\nu)^2) (eV )^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.067</td>
<td>0.3786</td>
<td>7.9239</td>
<td>2.703</td>
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<td>0.087</td>
<td>0.3793</td>
<td>7.9093</td>
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<td>63.99</td>
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<tr>
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</tr>
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<td>0.200</td>
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<td>7.8658</td>
<td>1.609</td>
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</tr>
<tr>
<td>0.300</td>
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<td>1.204</td>
<td>3.243</td>
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<tr>
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<td>7.8064</td>
<td>0.916</td>
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<td>0.511</td>
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<td>2.67</td>
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<td>0.700</td>
<td>0.3914</td>
<td>7.6648</td>
<td>0.357</td>
<td>3.174</td>
<td>1.28</td>
</tr>
</tbody>
</table>
Figure 4.10: Transmission spectrum of thicker film relative to thinner film.
Figure 4.11: A graph of $(h \nu \alpha t)^2$ against $h \nu$ for determination of energy gap of F:ZnO film.
4.3 CHARACTERIZATION OF ZnO:F / SiO₂ / p-Si SOLAR CELL

In this section, characterization of the deposited cell are discussed. The sheet resistance of the as-deposited cell was found to be 24KΩ. The cell was deposited at optimum conditions. After annealing the cell in vacuum, the sheet resistance at room temperature was found to be 390Ω. The I-V characteristics are presented in the next section.

4.3.1 I-V characteristics

The dark I-V characteristics and light I-V characteristics under 80mW/cm² insolation for the solar cell are shown in figure 4.12. The data for these characteristics are given in appendix B1 and B2. From the I-V characteristics in figure 4.12, the cell parameters were obtained (refer to section 3.8).

Short circuit current, \( I_{sc} = 1.41 \text{ mA} \)

Open circuit voltage, \( V_{oc} = 0.235 \text{ V} \)

The fill factor (FF) and efficiency were obtained using equations (56) and (57),

\[
\text{Fill factor (FF)} = 0.267 \\
\text{Cell efficiency, } \eta = 0.11\%
\]

The cell efficiency is low. This can be due to high thickness of the insulator layer and sheet resistance of the deposited film. It could also be attributed to high series resistance of the cell.

4.3.2 Determination of series resistance

Light I-V characteristics for ZnO:F / SiO₂ / p-Si solar cell at two different illuminations are shown in figure 4.13. The data for these illuminations are given in appendix C1 and C2. The series resistance of the cell was calculated using equation (60). The series resistance was found to be 83.3Ω.
Figure 4.12: Dark and light I - V characteristics under 80mW/cm$^2$ insolation.
Figure 4.13: Light I-V characteristics for two different illuminations.
CHAPTER FIVE

CONCLUSION AND SUGGESTIONS

5.1 CONCLUSION

Undoped and Fluorine doped zinc oxide thin films have been deposited by spray pyrolysis technique. The optimum conditions were established to be:
Substrate temperature 480°C, spray height 28 cm and carrier gas pressure was 8 lbf / in² (approximately 5.6 x 10⁴ N / m²). The electrical properties of the films were strongly influenced by the substrate temperature and the rate of flow of the carrier gas (nitrogen).

Fluorine doped ZnO films, deposited at optimum conditions exhibit attractive transparent conducting properties. A film of thickness 0.476μm gave a visible transmittance of about 82% and sheet resistance of about 270 Ω/□. It was observed that fluorine doping produced higher transparency and conductivity. Doping of 1.5% fluorine produced the best electrical conductivity. The sheet resistance produced is high compared to resistance of less than 15 Ω/□ which have been reported by other workers. This is due to the resistance between the film and the contacts and also the purity of the used chemicals.

The effects of air and vacuum annealing of the undoped and fluorine doped ZnO films on the electrical properties were also of interest. These effects were attributed to the creation and annihilation of extrinsic trap states localized at the grain boundaries, which then result from the chemisorption and desorption of oxygen at the grain boundaries. Annealing of the films also gave higher transmittance and the absorption shifted to the higher energies.

It was observed that ZnO films exhibit a direct band gap of 3.24 eV which is comparable to the values obtained by other workers. The wide band gap, high transmittance in the visible region and high conductivity of the fluorine doped ZnO film make it ideal for application as window material for solar cell.

The fill factor and efficiency of ZnO:F /SiO₂ / p-Si solar cell was found to be 0.267 and 0.11% respectively. The low value of efficiency obtained could be due to thick insulator layer and high series resistance (high sheet resistance). Poor contacts and junction effects could also contribute to the low efficiency obtained. However, this efficiency is comparable to other
cells fabricated in our research laboratories. The efficiency is much lower than that obtained for SnO₂:F / SiO₂/n-Si solar cell reported by Singh et al [50].

The spray pyrolysis experiment is easy to set using locally available materials and is inexpensive and easy to use. The major challenge of this technique is to minimize the high porosity and gross texturing that is associated with volume shrinkage. Film contamination during deposition and evolution of dangerous gaseous by-products is also a major challenge.

5.2 SUGGESTIONS

In the course of this work, observations have been made that could lead to fabrication of films with good electrical and optical properties. The sheet resistance of the films obtained was high and needs to be reduced further for improved performance of the films. This can be obtained by:

1. Modifying the spray pyrolysis apparatus especially the dimensions of the nozzles.
2. The spray pyrolysis apparatus could be designed in such a way that it be fitted together with a vacuum unit so as to avoid contamination of the films by impurities.
3. The chemical used should be analytical grades (pure)

Work should also be done on determination of optimum conditions for the ZnO thin film deposition especially the gas flow rate and substrate temperature. A means of measuring the oxide layer thickness on the silicon wafer is necessary so as to improve the cell performance. This could be measured easily if the ellipsometry instruments were available. To optimize the performance of the cell, the resistance of the metal-semiconductor boundary should be eliminated by reducing the grain-boundary effects.
REFERENCES

APPENDICES.

A1: Values of thermoelectric effect for 1.5% fluorine doped ZnO film

<table>
<thead>
<tr>
<th>Ambient temperature (K)</th>
<th>( \frac{1000}{T} ) (1/K)</th>
<th>( \Delta T ) (K)</th>
<th>( \Delta V ) (μV)</th>
<th>( S = \frac{\Delta V}{\Delta T} ) (μV/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295.90</td>
<td>3.380</td>
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<td>2400</td>
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<td>298.50</td>
<td>3.350</td>
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A2: Values of thermoelectric effect for 2.0% doped ZnO film

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<th>ΔT (K)</th>
<th>ΔV (μV)</th>
<th>S = ΔV / ΔT (μV / K)</th>
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<td>305.5</td>
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<td>306.9</td>
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<td>3000</td>
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<table>
<thead>
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<th>ΔT (K)</th>
<th>ΔV (μV)</th>
<th>S = ΔV / ΔT (μV/K)</th>
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### B1: Dark I-V characteristics for ZnO:F / SiO$_2$ / p-Si solar cell.

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<th>Voltage (V)</th>
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<tr>
<td>0.006</td>
<td>0.00</td>
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<tr>
<td>0.052</td>
<td>0.02</td>
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</tr>
<tr>
<td>0.156</td>
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<td>0.205</td>
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<td>0.248</td>
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<td>0.272</td>
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<tr>
<td>0.320</td>
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</tr>
<tr>
<td>0.354</td>
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<td>0.390</td>
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</tr>
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<td>0.425</td>
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</table>
### B2: Light I-V characteristics under 80mW / cm² insolation.

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<th>Voltage (V)</th>
<th>Current (mA / cm²)</th>
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<td>0.000</td>
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</tr>
<tr>
<td>0.120</td>
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<td>0.147</td>
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C1: Light I-V characteristics for lower illumination

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<thead>
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C2: Light I-V characteristics for higher illumination.

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<td>-0.68</td>
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<tr>
<td>0.110</td>
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<tr>
<td>0.145</td>
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<td>0.158</td>
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<td>0.165</td>
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<td>0.196</td>
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D: Annealing in air and vacuum.

<table>
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<th>Temp. (°C)</th>
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<th>Cooling $R_{sc} \ (K\Omega)$</th>
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