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CHARACTERISATION OF HYDROGENATED AMORPHOUS SILICON A-SI:H SOLAR CELLS USING IMPEDANCE SPECTROSCOPY (IS)

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This thesis is presented for the degree of

Master of Philosophy of

Murdoch University Western Australia

July 1998
I declare that this thesis is my own account of my research and contains as its main content work which has not previously been submitted for a degree at any tertiary education institution.

........................................

A. BABAN
TO MY PARENTS,
ABSTRACT
Practical applications of hydrogenated amorphous silicon (a-Si:H) solar cell are increasing significantly, because of their versatility, reduced cost and improved efficiency. The purpose of this work was to experimentally examine the performance and degradation of p-i-n junction a-Si:H solar cells. The samples were fabricated by glow discharge (GD) technique often called plasma enhanced chemical vapour decomposition (PECVD). The simple p-i-n photovoltaic cells were prepared at a pressure of 0.1 torr and a temperature of 225°C on untextured glass substrates. The cells used were just over 5% efficiency and were made under deposition conditions that yield cells in the range 5% to over 7% efficiencies.

To investigate the performance and degradation of the cells, we have measured the current-voltage characteristic curves for each case, dark and illumination. The cell's internal parameters, short circuit current (Ish), open circuit voltage (Voc), fill factor (FF), and the efficiency (\( \eta \)), as well as the series and the shunt resistances were calculated from the measurements.

The microscopic mechanisms and generation of electron/hole pairs in a-Si:H photovoltaic cells were studied by employing the technique of impedance spectroscopy (IS). The complex impedance measurements as a function of frequency and bias voltage have been used to derive the parameters of the equivalent circuit. The results showed that over a limited range of frequencies and bias voltages, an equivalent circuit composed of a shunt resistor and a capacitor is adequate to describe the measurements. Otherwise, the simple equivalent circuit model requires modification and may be interpreted by assuming that the values of one or more of the equivalent circuit elements are a function of frequency. We have related this microscopic model to the microscopic mechanisms within the material; the density of states and the generation lifetime of both electrons and holes. The measurements based on the potential of impedance spectroscopy (IS) technique to distinguish between
processes that proceed at different rates, indicated that the mechanisms leading to generation of electron/hole pairs may be identified.

To probe the stability of the cells, we have light soaked the samples for up to 60 hours by exposing them to simulated AM 1.5 global illumination. The resulting reduction in short circuit current and fill factor caused a significant decline in the efficiency while the open circuit voltage remained relatively constant. The efficiency decline was assessed in terms of current density and fill factor loss. The deterioration of the cell’s performance was attributed to creation of a large number of defect states in the bulk that reduce the minority carrier lifetimes in the i-layer. Annealing at 180°C for 60 minutes restored the initial efficiency.

The capacitance-voltage measurements were performed in dark and illumination to investigate the deep defect mechanisms and detect the transitions within the depletion region by varying the d.c bias voltage. Photocapacitance of the charged carriers were determined from the values of capacitance in the dark and illumination. The photocapacitance was used as a measure of internal field change and recombination process.

Sub-bandgap energy photons can produce electron/hole pairs that may contribute to the primary photocurrent and improve the efficiency of the cell. This was investigated through illuminating the sample with red or infra red light (650nm and 950nm respectively). The results from these measurements were interpreted as being due to one or both of the suggested processes; the transition caused by multiple photons, or/and as a result of illumination the band tail states extend into the forbidden gap to an extent that a single photon is sufficient to stimulate an electron from the upper level of valence band tails to the lower conduction band tails.

The results from this study have provided valuable information about decay/recombination, the minority carrier lifetimes in the i-layer which limit the performance of the material, and production of photogenerated carriers under photon energies less than the optical gap. This information could lead to the production of devices with improved efficiencies.
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CHAPTER 1

INTRODUCTION

1.1. Sources of Energy and Their Development

Limited availability and serious pollution risks are the main reasons behind the inability of either fossil or nuclear fuel to be considered as an energy source beyond the immediate future. The search for an alternative energy source was especially concentrated following the oil crisis of 1973. Solar energy undoubtedly is environmentally clean, practicable, endless and convenient. Considerable interest in employing photovoltaic solar power to replace other sources of energies has emerged to produce a reliable commercial product in a remarkably short period of time. Programs of research, development and demonstration have been set up and the space program of the 1960's gave tremendous inputs to the development of solar cells, and brought the technology to a point where it could be seriously considered for terrestrial power supplies [Hilger, 1991].

Since the 1960's, the idea of producing electricity directly from sunlight has attracted the attention of scientists on the one hand, and public imagination on the other hand, and each decade has seen photovoltaic development and high reduction of costs due to improvements in the efficiency and has led pv cells to be considered as a permanent source of energy. The current decade has seen the biggest boost in remote-area photovoltaic power system markets in developed countries because of cost competitiveness due to their versatility. No doubt the next century will become
the greatest photovoltaic development market we have ever seen and this form of energy generation will take over all sources of energy.

A solar cell is a photovoltaic device designed to convert sunlight into electrical power and deliver this power into an adequate load in an efficient manner using the electronic properties of a kind of material called a semiconductor. Among the many semiconductor materials used for solar cells, a-Si:H has attracted much more attention than others because of low costs and unique electronic and optical properties. These photovoltaic systems appears to be one of the most promising ways of meeting the increasing energy demands of the future in a time when conventional sources of energy, coal, petroleum and natural gas, are costly, inefficient, and being reduced.

The world’s largest solar village is being designed in Sydney for the Olympic games in the year 2000 [Green, 1997]. Over 600 apartment homes according to the author, will be built with their own network of integrated photovoltaic system providing a massive amount of electricity needs. This Olympic village, which will be the legacy of photovoltaic systems in Australia and the world, will generate one million kilowatt hour per annum. The cost of each kilowatt is expected to be equal to conventional power cost and running the homes will be cheaper in terms of electricity cost.

1.2 Amorphous Silicon

Amorphous silicon has attracted particular attention since its discovery in 1969 [Hamakawa, 1982] because of the following reasons:
I) Energy requirements in manufacturing the a-Si solar cells are much less than that for the single crystalline silicon solar cells because of its low growth temperature (200-400°C). This reduces the energy pay back period.

II) The optical absorption coefficient of the a-Si is greater than $10^{-4} \text{cm}^{-1}$ over the visible region of the solar spectrum, so that an efficient solar cell can be constructed with a thin film of about 1 $\mu$m in thickness that absorbs as much light as 50 $\mu$m of its crystalline counterpart. The key issues of improving efficiency in a-Si solar cell is shown in figure 1.1.

![Figure 1.1. Key issues for raising the efficiency of a-Si:H single junction solar cells [after Konagai, Brodsky 1987]]
III) A large area solar cell can be easily realised because the a-Si film is deposited by the plasma decomposition of silane (SiH₄) on an inexpensive substrate, such as sheet metal or glass plate.

V) The fabrication processes of the a-Si solar cells are much simpler in comparison with those of crystalline solar cells and have a greater potential for automation.

Unhydrogenated amorphous silicon was prepared by sputtering or by thermal evaporation before the discovery that the incorporation of hydrogen would reduce the defect density of the material and improve doping, conductivity and produce the desirable characteristics of a useful semiconductor.

Chittick 1969 [Chittick et al., 1969] was first to announce the fabrication of a hydrogenated amorphous silicon (a-Si:H) thin film using glow discharge as the deposition technique. In glow discharge which referred to as plasma enhanced chemical vapour deposition, the silane gas (SiH₄) is excited by an electrical plasma which causes the gas molecules to dissociate and deposit on heated substrates.

The substrate temperature during the deposition is usually between 200-300°C and the feed-gas pressure is between 0.1-1 torr. This material can be doped to be p-type or n-type, over a wide range of conductivity. The addition of a small quantities of phosphine (PH₃) or diborane (B₂H₆) to the deposition gas (SiH₄) results in an increase in the room temperature conductivity more than seven orders of magnitude and reduces the activation energy from 0.75eV in undoped amorphous material to 0.15eV with phosphorus doping and 0.3eV for boron [Spear and LeComber, 1977].
Subsequent measurements of conductivity, thermo power and mobility all indicated that Fermi-energy \( E_F \) shifts towards the valence band edge for p-type and shifts towards conduction band for n-type [Knights et al., 1979]. This process incorporates hydrogen into the material, apparently in such a way that it satisfies some of the dangling bonds. The effective role of hydrogen is to considerably reduce the defect density, which significantly improves electronic properties of the material [Lewis et al., 1974].

1.3 The Role of Hydrogen in a-Si:H

Amorphous semiconductors are recognised by the absence of long range order and the presence of dangling bonds in their structure. As a result the abrupt band edges of the crystalline states are replaced by a broadened tail of states extending into the forbidden gap, which originates from the deviations of the bond length and angle arising from the long range structural disorder [Street, 1991]. Dangling bonds are defects in the mobility gap which act as recombination centres. The density of defect states (DOS) in amorphous silicon is about \( 10^{19} - 10^{20} \, \text{spin/cm}^3 \) and this determines the optical and electronic properties by controlling trapping and recombination.

The role of hydrogen in the a-Si:H solar cell is to passivate the defects on the band gap by replacing the weak Si-Si bonds with Si-H ones. The effect of the vast majority of hydrogen bonds \( (10^{21} \, \text{atoms/cm}^3 \) in a typical a-Si:H sample) is to reduce the defects and improve the efficiency. The high efficient solar cell can be produced by reducing the DOS to less than \( 10^{17} \, \text{spin/cm}^3 \) [Smith et al., 1987]. Jackson and
Amer had found that a good hydrogenation could lead to reduction of DOS by five orders of magnitude [Jackson et al., 1982]. They also found that the Fermi level is changed with hydrogen concentration ($C_H$). For 20% $C_H$, the Fermi level has moved by 0.25eV.

The optical and electronic properties of the resulting films (a-Si:H) are influenced significantly by hydrogenation. Increasing the bonded hydrogen content in the network leads to a wider optical gap of that cell by eliminating the states at the top of the valence band [Yamasaki et al., 1989]. The dark conductivity and the photoconductivity are also affected by $C_H$ for a typical a-Si:H solar cell. The dark conductivity decreases more than seven orders of magnitude for a cell containing 40% $C_H$, while the photoconductivity reduces by one order of magnitude for the same $C_H$ rate [Pinarbasi et al., 1990].

Although the highest efficiencies that cells based on a-Si:H have reached to date is much below those for crystalline silicon and polycrystalline silicon solar cells, it is possible to produce modules of comparable price per unit power output. Reduction of costs continue particularly as production increases allow lower fabrication expenses. For instance, in 1956 crystalline solar cells cost $350 US per peak watt [Bube, 1983]. A massive reduction in the price reached $15 US per peak watt by 1977. The cost has continued to decrease to only $0.5 US per peak watt by 1990 using a-Si:H solar cells. Further reduction is expected to module costs below the current levels by early next century.
The possible utilization of hydrogenated amorphous silicon as a solar cell material has received considerable attention, not only for low cost and large area, but for its various applications. These including image pick up tubes, image testing arrays, as well as electronic devices such as transistors, diodes, and electrophotographic drums [Hamakawa, 1982]. The favourable properties of this material are its high absorption coefficient and optimum band-gap. Table.1 shows some proposed applications of amorphous silicon. Most of these products are commercially available.

<table>
<thead>
<tr>
<th>Image pick-up tube</th>
<th>DIFETs</th>
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<tbody>
<tr>
<td>Strain gauges</td>
<td>LEDs</td>
</tr>
<tr>
<td>Optical recording</td>
<td>FETs for ambient sensors</td>
</tr>
<tr>
<td>Fast detectors and modulators</td>
<td>Passivation layers</td>
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<tr>
<td>Diodes</td>
<td>Charged-coupled devices</td>
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<td>Memories</td>
<td>Bipolar transistors</td>
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<tr>
<td>Photolithographic masks</td>
<td>Optical waveguides</td>
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<tr>
<td>X-ray detectors</td>
<td>Optically modulated neural networks</td>
</tr>
<tr>
<td>Charge particle detectors</td>
<td></td>
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</table>

**Table 1.1.** Proposed application of a-Si:H (after Le Comber, 1989).
Open-circuit voltage ($V_{oc}$), short-circuit current ($I_{sc}$), and fill factor (F.F) are the most important parameters to examine solar cell behaviour [Hovel, 1975]. These parameters determine the cell efficiency and the circuit conditions which can provide the best sample. The higher the fill factor, open-circuit voltage, and short-circuit current the more efficient the cell and the better the quality of the cell as we talk about these parameters in detail in later chapters.

Efficiency improvement has been seen as a major factor to the success of the glow discharge a-Si:H solar cell domination. The initial conversion efficiencies of 2-3% were obtained by Carlson and Wronski in 1976. Following this, improved efficiencies were reported from other groups, the cell efficiency had increased by 1% each year to 12-14% by 1989 [Street, 1991].

The mobility and lifetime of minority carriers are of importance in determining the performance of a-Si:H solar cells. The lifetime depends on the illumination level, reflecting the displacement of the electron quasi-Fermi level and change in carrier recombination kinetics. Minority carrier lifetime for a-Si:H solar cells has been investigated by several methods. Among those techniques open-circuit voltage decay (OCVD), which was originally used by Mahan [Mahan et al., 1979], deep level transient spectroscopy (DLTS) by David Cohen and co-workers [Cohen et al., 1987], Capacitance-Voltage measurements [D. V. Lang et al., 1982].

The densities, energies, and types of states present in the gap of a-Si:H play an important role in device performance [Fonash, 1991]. These gap states depend both on deposition conditions and subsequent treatments. The density of valence band
states has been studied by photo-emission techniques, such as Ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy. However, the density of gap states $g(E)$ has been studied by various methods such as field-effect method, capacitance-voltage (C-V) method and deep-level transient spectroscopy (DLTS) [Lang et al., 1982], [Cohen et al., 1987]. A very new technique used in the study of a-Si:H solar cells, is that of impedance spectroscopy (IS). This technique is widely used in electrochemistry to investigate electrode processes [Sluyters-Rehbach and Sluyters, 1970].

Despite the fact that the a-Si:H technology developed rapidly, and lent itself to large scale industrial production as a low cost technology, there are two major problems still facing a-Si:H solar cell: the efficiency limit and optical degradation. Light induced degradation in a-Si:H solar cells was shown by Staebler and Wronski for the first time in 1977 [Staebler and Wronski, 1977]. Subsequent work [Staebler et al., 1980] showed that the performance of amorphous silicon also decreased by prolonged exposure of light and degradation could be reversed by annealing [Lang et al., 1982], [Joannopoulos and Lucovsky, 1983], [Fortmann et al., 1988], [Charles Lee et al., 1985], [Street, 1991]. Carlson showed recently that the annealing process is accelerated by using reverse bias voltage during the annealing [Carlson and Kamala Rajan, 1997]. This degradation is a big issue in acceptance of a-Si:H solar cells and is still under investigation to find a breakthrough for this problem.

In spite of great progress in fabrication and efficiency of a-Si:H solar cells, such cells have not reached the levels of other semiconductors in those regards. Practically
there is yet a long way to go for this kind of material to satisfy the literature expectations; if a cell with maximum internal parameters can be fabricated, then undoubtedly the highest efficiency a-Si:H solar cells could be achieved.

1.4 The Aims

In spite of the permanent improvements in the production of a-Si:H solar cells, cells based on a-Si:H have not yet attained the levels of efficiency, and stability needed for their comprehensive adoption. This may be due to lack of fundamental understanding about the a-Si:H materials and their behaviour in the device. This project aimed to obtain crucial information needed to understand physical, optical, structural, and transport properties (drift and diffusion), of solar cells. Experimental investigations of a-Si:H solar cells are the purpose of this project with the following objectives:

- To obtain a greater understanding about the performance and stability of a-Si:H solar cells by investigating the production, transport (drift and diffusion), and decay/recombination of the charge carriers.

- To model the solar cell as an equivalent circuit and determine its parameters which are crucial to describe the performance of the device.

- To distinguish between processes (fast and slow) that proceed at different time scales.

- To probe the degradation of photovoltaic cells with light soaking and their recovery after annealing.
Assessment of sub-bandgap transition at low light intensity and the production of current carriers by the interaction of multiple sub-bandgap photons.

1.5 Organisation of The Thesis

Chapter two gives a short general theory relevant to the basic concepts and principal physical mechanisms in p-i-n junction a-Si:H devices. It also presents an insight into methods used for sample preparation, modeling and parameters of the equivalent circuit, photodegradation, and some techniques used for the characterisation of a-Si:H solar cells.

Chapter three presents a comprehensive description of the fundamental aspects of the impedance spectroscopy technique, application to a-Si:H, theoretical measurements, circuit modeling, and effect of external parameters (bias voltage) on the impedance of the solar cell.

Chapter four describes the experimental details: sample preparation, apparatus, deposition process, aluminium contact deposition, I-V characteristic measurement curves, and experimental procedure and arrangements of the impedance spectroscopy technique.

In chapter five the experimental results are presented including curves and plots of impedance achieved in this project and explanations. The results are compared to previous work done on impedance spectroscopy.

Finally, chapter six discusses the results and suggests further work for future.
2.1. Introduction.

The behaviour of a solar cell is influenced strongly by the technologies that are used in making the cell, and the optimum design for a device depends on the application for which it is intended. N on P silicon cells incorporated with some other elements might be used for space application, because of the high radiation tolerance of that device [Hovel, 1975]. For terrestrial applications, thin film silicon is the best option as it possesses the highest efficiency per unit cost figure which is necessary to make solar cells financially competitive with other methods for generating large amounts of power.

The effect of hydrogen on the electronic properties of silicon has proved to be more subtle in n-type than in the p-type material [Jacques et al., 1991]. The passivation of deep level defects and shallow impurities in semiconductors by hydrogen has been studied extensively in the last decade. Various techniques have been used to probe the passivation of defects, between them; local vibrational model technique, Uniaxial stress technique, IR absorption studies, and Raman Spectroscopy.
2.2. The Physical Concept of Amorphous Silicon

2.2.1. The Nature of Amorphous Silicon

a) Pure Amorphous Silicon (a-Si)

Amorphous silicon is a semiconductor tetrahedrally coordinated and recognised by the absence of long-range order due to large deviations in the bond angles as well as the presence of unsaturated “dangling” bonds. This disorder of the atomic structure is the main feature which distinguishes amorphous silicon from crystalline materials as may be seen in figure 2.1.

![Figure 2.1](image)

a) Crystalline silicon.  

b) Amorphous silicon.

Figure 2.1. Dimensional illustration contrasting the difference between a) crystalline and b) amorphous silicon networks.

The structural disorder in a-Si results in a broadened tail of electronic states in both valence and conduction bands extending into the forbidden gap replacing the abrupt band edges in crystalline silicon. Figure 2.2 shows schematic density of states for crystalline and amorphous silicon.
Figure 2.2. The schematic density of states distribution for: a) crystalline silicon and b) pure amorphous silicon showing the bands, the band tails, and defect states in the band gap.
Density of states (DOS) is the number of states per unit volume in the mobility gap between valence and conduction bands. Without the constraint of periodicity, it is difficult for each silicon atom to be linked up with four others. This nature of the amorphous silicon increases the number of unsatisfied “dangling” bonds within the structure of the material. These unsaturated dangling bonds associated with defects in pure amorphous silicon structure, which are in order of $5 \times 10^{19}$ free spins $cm^{-3}$, give rise to additional unwanted energy states for electrons within the normally forbidden band-gap between conduction and valence electrons. So, the band edges are not well defined which are important in determining the width of the band tail. These are the main features that distinguish amorphous from crystalline materials and are significant in semiconductors because of the effects on the electronic, optical and vibration behaviour. These dangling bonds ($10^{19}$ spin $cm^{-3}$) in the mobility gap of pure amorphous silicon act as trapping and recombination centres which in turn limit the minority carrier lifetime and thus, no photovoltaic properties are observed [Green, 1982].

Amorphous silicon can be doped to form p-n junctions through deposition from silane ($SiH_4$) by the glow discharge technique [Street, 1991]. The hydrogen concentration in the film during the deposition, created when the silane decomposes, is usually around 5-10%. During the growth a silicon atom may be bonded to one, two, or three hydrogen atoms as is shown in figure 2.3.
b) Electronic Properties

The description of the electronic properties of semiconductors directly depends on its energy distribution of electronic states. The different states determine the electrical transport, recombination process and doping. In crystalline semiconductor, the abrupt termination at the valence band maximum and the conduction band minimum
is the main distinguishing aspect of the density of states; due to sharp edges in the density of states from a well-defined forbidden band-gap [Nagel, 1988]. The presence of this band-gap, however, between occupied valence band and empty conduction band is one of the fundamental properties of a semiconductor. The band-gap model for an amorphous semiconductor assumes that there is a tail of localised states extended into the forbidden gap, which originated from the deviations of the band length and the angle arising from the long range structural disorder [Street, 1991]. These band tails are very important despite their relatively small concentration, because electronic transport occurs at the band edges.

2.2.2. Hydrogenation or (The Role of Hydrogen)

The role of hydrogen in a-Si:H is to passivate and eliminate dangling bonds in amorphous silicon and break weak Si-Si bonds. Hydrogen reactions control the structure through chemical reactions between H and Si. A significant enhancement in optical and electronic properties is noticed after the addition of hydrogen to pure silicon. The photoconductivity is improved by seven orders of magnitude and dark conductivity by eight orders of magnitude [Spear and LeComber, 1975]. The improvement of conductivity was confirmed by subsequent experiments [Spear and LeComber, 1977] as a result of a shift in Fermi energy level in the mobility gap, and that n-type and p-type conduction occurring. The hydrogenation has reduced the density of states due to dangling bonds by almost four orders of magnitude in pure amorphous silicon. This decrease in DOS increases the minority carrier lifetime and
enhances the photoconductivity. Cells with low DOS lead to a high efficiency and perform better while cells with high DOS perform poorly.

It was proposed by Street [Street, 1988] that the structure of plasma-deposited amorphous silicon is controlled by hydrogen reaction near the growing surface. The incorporation of hydrogen not only passivates the existing dangling bonds but also breaks weak Si-Si bonds and forms Si-H bonds [Ching et al., 1979]. The attachment of hydrogen to a silicon dangling bond is shown in reaction below

\[
Si \cdot + H \leftrightarrow Si - H
\]

The hydrogen weak Si-Si bond reaction depends on chemical potential of the hydrogen in the plasma. Weak Si-Si bonds that lie below the hydrogen chemical potential, are broken while stronger bonds remain.

\[
H + (Si - Si)_{\text{weak}} \leftrightarrow Si - H \cdot Si
\]

The intrinsic disorder of the amorphous network results in localised states that comprise the band tails that extend into the mobility gap. The weak Si-Si bonds contribute to states in the middle of the bands, while states near the mobility edge can still provide “extended state” conduction of charge carriers. In contrast, states located under the band edge have lower mobility, and transport occurs by thermally activated hopping. The more distorted the weak Si-Si bonds the deeper from the
band edge in the mobility gap will the state reside. Studies of localised gap states [Madan et al., 1976] found that the incorporation of hydrogen lowers the density of band tail states and sharpens their distribution in energy as indicated in figure 2.4.

![Figure 2.4. Sketch of the energy dependence of the density of states for unhydrogenated a-Si and a-Si:H [After Madan et al., 1976].](image)

The concentration of bonded hydrogen in a-Si:H films is of the order of $5 \times 10^{21} \text{cm}^{-3}$, exceeding by two orders of magnitude the dangling bonds found in pure amorphous silicon films. Hence, the excess Si-H bonds can only result from the breaking of weak Si-Si bonds as there are not enough dangling bonds in the film to absorb the extra hydrogen. Hydrogen can also reform weak Si-Si bonds into strong Si-Si bond through indirect involvement in the reaction, as stated below
\[(Si - Si)_{\text{weak}}^\text{weak} \ (H) \leftrightarrow (Si - Si)_{\text{strong}}^\text{strong} \ (H)\]

A combined reaction of hydrogen being liberated from a-Si:H bond and breaking a weak bond is shown in the schematic diagram below.

![Schematic illustration of a possible hydrogen reaction in which hydrogen is released from a-Si:H bond and breaks a weak Si-Si bond causing two defects [after Street 1991].](image)

These and other similar reactions allow the hydrogen to influence the dangling bond and weak bond density and provide a mechanism for hydrogen to modify the electronic structure during the growth of films. However, using amorphous silicon-hydrogen (a-Si:H) alloy displayed significantly larger band gaps than crystalline silicon and was also much more absorbent. This gives more opportunity to films as thin as 1μm to be used.
2.2.3. The Density of States (DOS)

The band-gap states arise from departures of the ideal network, such as coordination defects which determine many electronic properties by controlling trapping and recombination. The density of states (DOS) in semiconductors is defined as below:

\[ N(E) = \frac{8\sqrt{2}\pi m^2 e'}{h^3} \left( E - E_i \right)^{\frac{1}{2}} \ldots \ldots \ldots (2.1) \]

Where \( h \) is Plank's constant and \( E_i \) is the ground electron energy state.

This expression can be used for both valence and conduction bands. The probability of occupation of these energy states may be written as:

\[ f(E) = \frac{1}{1 + e^{\left( E - E_F \right) / kT}} \ldots \ldots \ldots (2.2) \]

\( k \) is Boltzman's constant and \( T \) is the absolute temperature. The number of electrons in the conduction band per unit volume of the crystal, \( n \), is given:

\[ n = \int_{E_c}^{E_{\text{max}}} f(E)N(E)dE \ldots \ldots \ldots \ldots \ldots \ldots (2.3) \]

Since \( E_c \) is many kTs larger than \( E_F \) then, the \( f(E) \) of the conduction band is reduced to

\[ f(E) = e^{-\left( E - E_F \right)/kT} \ldots \ldots \ldots (2.4) \]
From equation 2.2, 2.3, and 2.4 $n$ and $p$ can be written as:

$$n = N_e e (E_f - E_c) / kT \quad (2.5)$$

$$p = N_e e (E_v - E_f) / kT \quad (2.6)$$

Where $p$ is the total number of holes in the valence band per unit volume, $E_f$ is Fermi energy level and lies close to midgap in a pure and perfect semiconductor. Fermi level $E_f$ moves away from midgap and approaches the conduction band as the semiconductor becomes more heavily doped for n-type material or valence band for p-type material. This is illustrated in figure 2.6.

**Figure. 2.6.** Energy of the Fermi level as a function of the concentration of donors and acceptors [After Green 1982].
2.3. Hydrogenated Amorphous Silicon Solar Cells

Semiconductors, pure or doped, p-type or n-type, are bilateral; the current flows in either direction with equal facility. If, however, a p-type material was brought in intimate contact with an n-type material, initially the mobile carriers diffuse across the junction due to the carrier density gradient. As a result an electric field is produced in opposite direction of the diffusion current to prevent further diffusion of electrons. Eventually, a dynamic equilibrium is established when the energy levels have shifted so that there are equal numbers of carriers on either side of the junction, electrons in the p-side and holes in the n-side. The resulting device is called a p-n junction and the narrow layer or region where the carriers are accumulated is called the depletion region, as may be seen in figure 2.7.

![Figure 2.7. Basic structure of a p-n junction.](image)

Illumination excites the electrons from the valence band by providing them with photon energies higher than the optical gap and reach into the conduction band. The carriers that arrive at the junction before they are trapped will be swept away to the
n-side under the effect of the induced electric field. Thereby, the density of electrons in the n-side and holes in the p-side are increasing inducing a potential difference across the device. This is the principle of photovoltaic solar cells. The conductivity of the material can be increased by adding small amount of impurities in the process called doping. Adding a small amount of a trivalent element, such as boron, to pure silicon produces p-type semiconductor, while adding a small amount of pentavalent element, such as phosphorus, to pure silicon produces n-type semiconductor. The boron called acceptor and the phosphorus called donor in this case.

The diffusion current is proportional to the concentration gradient \( \frac{dn}{dx} \). The density of this current due to the presence of electrons is given by

\[
J_n = qD_n \frac{dn}{dx} \quad \text{(2.7)}
\]

When the concentration gradient at the junction is obtained, holes diffuse from the p-type material to the right across the junction into the n-region and recombine with some of the many free electrons in n-type material. Similarly, electrons diffuse from n-type material and recombine at the p-region with unoccupied holes. This will create an imbalance in the device. Under the action of the electric field, the opposite action occurs. When a p-n junction is under the action of the electric field, electrons drift across the junction randomly in an opposite direction to the field [Smith et. al., 1987]. These electrons collide with lattice atoms or impurity atoms, or defects in the crystal structure. The electron carrier mobility can be written as:
\[ \mu_e = \frac{\nu_e}{E} = \frac{q t_r}{m_e} \quad \text{(2.8)} \]

\( q \) = electron charge, \( t_r \) = relaxation time, and \( m_e \) = electron mass.

The corresponding current density flow due to the presence of conduction band electrons is:

\[ J_e = q n \nu_e = q \mu_e n E \quad \text{(2.9)} \]

The current hole density in the valence band is:

\[ J_h = q p \nu_d = q \mu_h p E \quad \text{(2.10)} \]

The conductivity of the device is given by

\[ \sigma = \frac{1}{\rho} = \frac{J}{E} = q \mu_e n + q \mu_h p \quad \text{(2.11)} \]

Amorphous silicon solar cells are usually made as p-i-n junctions. Unlike crystalline silicon, this material is of limited use without the undoped layer, simply because charge collections occur in the i-layer. There are different designs and configurations of p-i-n junction structures. The most common types are shown in figure 2.8.
In type (2) configuration, the device is made from a glass substrate which is coated with ITO (Indium Tin Oxide) and a thin layer of cermet (Pt-SiO$_2$) to provide a good electrical contact to the boron ($B_2H_6$) doped layer (P-layer = 10nm). The undoped (i) layer is the largest which is about 600-800nm thick followed by 20nm phosphorus ($PH_3$) doped layer (n) and finally, a metal such as Ti/Al (100nm) to form a back contact to the n-layer. A typical p-i-n junction a-Si:H diode is about 1μm thick which is 50 times thinner than the p-n junction of crystalline solar cells.

The light passes into the structure of the cell through the glass substrate and then through transparent conducting oxide (TCO) into the p-layer. This layer absorbs 30% of the incident light due to large absorption coefficient of doped layers. A schematic diagram of a p-i-n a-Si:H solar cell is illustrated in figure (2.9). The doped layers (p and n) induce a built-in potential across the junction as a result of diffusion.
layers (p and n) induce a built-in potential across the junction as a result of diffusion of the charged carriers to the contacts. The photoexcited carriers in these layers contribute nothing to the collection efficiency, because of the low minority carrier lifetime as a result of high defect densities in doped materials. Hence, the doped layers must be kept as thin as possible to ensure efficient carrier collection in the i-layer. Moreover, the photogenerated electrons and holes in the i-layer are the only effective component of the conversion efficiency. This implies that the carriers obtained by excitation in the i-layer are effectively conducted to the external circuit whereas the trapped carriers in the p-layer are wasted. Therefore, the i-layer must be as thick as possible, but not thicker than the depletion region, to achieve a high quality p-i-n a-Si:H solar cell. The thick i-layer absorbs maximum flux of the incident photons and hence, leads to the conversion efficiency.

**Figure 2.9.** Schematic diagram of p-i-n sensor at zero bias shows internal field of the undoped layer and the built-in potential $V_B$ [after Street 1991].
The conversion efficiency of a p-i-n a-Si:H solar cell essentially depends on the device characteristics, \((J_{sc}, V_{oc}, FF)\) short circuit current density, open circuit voltage, and fill factor respectively. The maximum output delivered power density by the device is the product of the values of these parameters, and is expressed as

\[
P_{out} = V_{oc} \times J_{sc} \times FF, \quad \eta = \frac{P_{out}}{P_{in}}
\]

Efficient a-Si:H solar cells can be made only at substrate temperatures between 200-400°C. Samples fabricated in these temperature ranges possess high short circuit current \((J_{sc})\) because they have low defect densities in their structure. The increase in the \(J_{sc}\) is due to the reduction in the optical gap \((E_{op})\) and increase in the absorption coefficient \((\alpha)\) as well as the enhancement in carrier recombination lifetime [Carlson et. al., 1979] by contacting electrons on both sides of the device.

The fill factor can be increased by reducing the i-layer dangling bonds to a fifth of that used for normal cell [Matsuura 1985]. This leads to an improvement in the device’s efficiency. However, despite the fact that, the best achieved values of \(J_{sc}\), FF are 19mA, 0.76 respectively [Ma. et.al., 1993] and \(V_{oc}\) is 1040mV [Li, et. Al., 1993] for a single junction p-i-n a-Si:H solar cells, under AM 1.5 global illumination. The obtained conversion efficiencies of this kind of material have not exceeded 8%. If, however, these values could be achieved in the same cell an efficiency over 15% would be obtained. There are some loss mechanisms that occur in p-i-n a-Si:H solar cells which limit the performance of the device. These
limitations have been studied by several groups [Carlson et al., 1979, Matsuura, 1985, Madan et al., 1979]. Firstly, diffusion of the minority carriers gives rise to a dark current [Carlson, 1977, Staebler and Wronski 1977]. The dark current density is expressed as

\[
J = J_0 \left[ \exp\left(\frac{qV}{nkT}\right) - 1 \right]
\]

Where \(J_0\) is the saturation current density and \(n\) is the diode quality factor. The dark current is the major limitation of the p-i-n a-Si:H solar cells. Secondly, the i-layer localised states that are originated from the dangling bonds act as recombination centres which limit the carrier collection. Hence, these defects need to be minimised in order to improve the efficiency. The related density of states losses have been estimated to be about 15% of the total losses in amorphous materials [Crandall, 1981 and 1982]. Whatever the nature of recombination, the electric field of the i-layer plays a crucial role in the operation of the cell. Increasing the applied reverse bias voltage depletes the i-layer further as a result of enhancement of the internal field. This implies that the mobility lifetime is increased which is needed to obtain better fill factor. Thirdly, although the photovoltaic performance of a-Si:H solar cell is not affected by all impurities found in the glow discharge environment, a small amount of impurities such as \(H_2O, H_2S, GeH_4\) and \(PH_3\) severely restrict the photovoltaic performance of the cell. Films made from a discharge in \(SiH_2Cl_2\) and \(H_2\) yield cells which exhibit poor photovoltaic performance [Carlson et al., 1979, Brodsky, 1985]. Apparently, the presence of \(GeH_4\) impurities create defects in addition of
isoelectronic centres which causes degradation in the films. Small percentages of $H_2O$ create defects below the conduction band. Similarly, $PH_3$ gives rise to shallow donors.

2.4. Sample Preparation Methods

Although RF glow discharge was the only technique used for sample preparation in this work, we thought that it is necessary to mention some other techniques that have been used for fabrication of a-Si:H solar cells, before the discovery of plasma enhanced chemical vapour decomposition (PECVD).

2.4.1. RF or DC Sputtering Depositions

RF and DC plasma sputter depositions of a-Si and a-Si:H in planar diode system have been investigated since the early 1970’s. This technique is versatile and easily controlled for fabrication of a-Si material [Cornish, Jennings and Hefter 1992]. The most successful effort in solar cell device fabrication was announced by Moustakas in 1985 [Matsuda et al., 1985], who operated an RF diode sputtering system by using a sputtering gas mixture of hydrogen and argon to deposit the microcrystalline p- and n- layers and the a-Si:H i-layer of 5.5% efficient solar cell on a stainless steel substrate. The fabrication of narrow- and wide- bandgap amorphous alloys were achieved by different groups [Hauser, 1976, Paul et al., 1976, Luft and Tsuo 1993]. Good quality a-Si:H films were prepared by DC magnetron reactive sputtering in an argon and hydrogen atmosphere, for the first time by Pinarbasi [Pinarbasi et al., 1990]. The hydrogen content of these films was controlled independently by the
hydrogen partial pressure in the discharge and argon ion beam used to sputter silicon and hydrogen beams to hydrogenate the growing film. However, the unsatisfactory film quality, the slow deposition rate and comparatively high cost made this technique suitable to be used mainly for research purposes only.

Figure 2.10. Schematic diagram of RF sputtering deposition technique [After Cheah, Swee Hock, 1987, cited by Lund 1993].
2.4.2. Chemical Vapour Deposition (CVD)

Thermal chemical vapour deposition is normally referred to simply as CVD and this refers to vapour-phase deposition upon a heated substrate. This technique is widely used for growing epitaxial silicon thin films [Grove, 1967, Luft and Tsuo, 1993]. The CVD process can be extremely simple and low-cost. In a conventional CVD reactor the gas and the substrate temperatures are equal and silane decomposes on the substrate surface to produce Si:H. The problem with this approach is that the substrate temperature must be higher than 500°C for silane to achieve reasonable deposition rates. As a result, the films have a high defect density and poor electronic properties due to low hydrogen content and high dangling bond densities. This technique is still used, though less commonly, and several groups are working on improvement of hydrogen content.

2.4.3. Glow discharge or Plasma Enhanced Chemical Vapour Decomposition (PECVD)

Plasma Enhanced Chemical Vapour Decomposition (PECVD) is the most popular deposition technique for a-Si:H alloy. This technique is also called Glow Discharge deposition, because of the visible luminosity of the plasma glow region, which is mainly the result of the de-excitation of emitting molecular and atomic species contained in the plasma [Luft and Tsuo, 1993]. This method is extremely accurate and produces comparatively high deposition rates under various conditions and temperatures. The resulting films are of high-quality [Cornish, Jennings and Hefter,
The substrate temperature during deposition is usually between 200-300°C, and the feed gas pressure is between 0.1-1 torr. Plasma-assisted gas decomposition reduces the substrate temperature required for the deposition process. This lower substrate temperature makes it possible for sufficient hydrogen to be incorporated during the deposition. The growth conditions of a-Si:H films have so far been defined by a set of discharge parameters such as gas pressure, concentration of silane ($SiH_4$), flow rate, rf power, and substrate temperature [Hamakawa, 1982].

Optimisation of the processing growth conditions has been attempted by varying the discharge parameters over a wide range. In order to achieve further improvement in the physical properties of a-Si:H, one should clarify chemical reactions during the plasma decomposition quantitatively. This clarification should not be only regarding the compositions of excited molecules in the plasma, but also on the mutual interaction among the reactive species in the gas phase as well as on the surface. Figure 2.11 shows a schematic diagram of plasma enhanced chemical vapour decomposition apparatus.

During the growth, the formation of a-Si:H films from a silane plasma is achieved by electron impact dissociation of the feedgas; accelerated free electrons collide with the neutral radical molecules under the effect of a high electric field causing ionization and resulting in more electrons. Some of these electron impact reactions are tabulated below:
Table 2.1. Some electron reactions during the growth of a-Si:H films.

Figure 2.11. Schematic representation of the plasma-enhanced chemical vapour deposition process after Gallagher 1986, Luft and Tsuo 1993].

\[
e + \text{SiH}_4 \rightarrow \text{SiH}_4 + e
\]

\[
\text{SiH}_2 + H_2 + e
\]

\[
\text{SiH}_3 + H + e
\]

\[
\text{SiH} + H_2 + H + e
\]

\[
\text{SiH}_2^* + H_2 + e + e
\]

\[
\text{SiH}_3^* + H + e + e
\]

\[
\text{SiH}_3^- + H
\]

\[
\text{SiH}_2^- + H_2
\]
$SiH_3$ is the dominant radical under certain conditions; low flow rate, low temperature, and low radio frequency power. This dominant radical deposits a film with a high percentage hydrogen composition and produces good quality film. On the other hand, however, under different conditions when the silane diluted with argon and high RF power, the dissociation of hydrogen occurs by secondary processes. This mechanism reduces from the surface hydrogen which reacts with the new dominant radicals such as $SiH_2$, SiH, and Si. Thus, the resulting film is a film with high deposition coefficient rate (k) and poor electronic properties due to large number of weak silicon bonds at the surface. These ions and radicals may undergo secondary reactions which lead to formation of heavier particles as below:

$$SiH_4 + SiH_2 \rightarrow Si_2H_6$$

$$Si_2H_6 + SiH_2 \rightarrow Si_3H_8$$

Adsorption of species at the growing film surface, reactions and reconstruction that result in the release of hydrogen in the final film are also involved in the growth of a-Si:H films. These films obtain extra hydrogen atoms from the bulk and release some of these atoms at the surface. Some of these processes are illustrated in figure 2.12.

Finally, these larger molecules contribute to the film growth. Nevertheless, the excess of larger molecules could spoil the film producing samples with poor quality. Therefore, it is generally recommended to avoid these larger molecules.
### Single Radical Reactions

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<tr>
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<tr>
<td>$\text{(SiH}_3)_2 + 2\text{b}$</td>
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<td>$\text{SiH}_2 + 3\text{b}$</td>
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<tr>
<td>$\text{SiH}_2 + \text{B} + 2\text{b}$</td>
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<tr>
<td>$\text{A} + 2\text{b}$</td>
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### Two Radical Reactions

<table>
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<tr>
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<tbody>
<tr>
<td>$\text{SiH}_3 + \text{A} + 2\text{b}$</td>
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<tr>
<td>$\text{SiH}_2 + \text{b} + \text{B} + \text{A}$</td>
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<tr>
<td>$2\text{A} + \text{b}$</td>
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### Incorporation

- $\text{H}_2 + (\text{SiH}_3)_2 + \text{B} + 2\text{b}$
- $\text{H} + (\text{SiH}_3)_2 + 2\text{b}$

$\text{Si}_2\text{H}_6^+ + 3\text{b}$

$\text{Si}_2\text{H}_4^+ + 3\text{b}$

$\text{(SiH}_3)_2 + 2\text{b} + \text{SiH}_4'$

$\text{Si}_2\text{H}_4, \text{Si}_2\text{H}_2$ possible

#### Figure 2.12

Illustration of some of possible processes taking place at the a-Si:H surface during growth. A, B, and b represent an absorbed $\text{SiH}_3$, dangling bonds, and $\text{SiH}$ bonds respectively [after Gallagher 1986, Luft and Tsuo 1993].

### 2.5. Spectral Response

#### 2.5.1 Device Parameters

A sample of crystalline silicon of 1μm thickness would not absorb much light across the visible spectrum because of its indirect band-gap, whereas, the amorphous material absorbs most of the visible spectrum because of its high absorption coefficient $\approx 10^{-4}$. The current-voltage characteristic of p-i-n solar cell in the dark and under illumination is shown in figure 2.13.
Figure 2.13. I-V characteristic curves for a single junction a-Si:H solar cells [After Chopra et al., 1983].

The illumination shifted the curve downwards, and the intersections of the curve with the current and voltage axis are short-circuit current and open circuit voltage respectively. The short circuit current for an ideal diode can be written as:

\[ I_{sc} = I_s \left[ \exp \left( \frac{qV}{nkt} \right) - 1 \right] - I_{ph} \] \hspace{1cm} (2.12)

\( n \) is diode quality factor = 1

\( I_{ph} \) is the light generated current which is given by

\[ I_{ph} = A q G (L_e + W + L_n) \] \hspace{1cm} (2.13)
Where: \( W \) is the width of the depletion layer, \( A \) is the active area of p-n junction, \( L_e \) and \( L_p \) are diffusion coefficient of electron and hole respectively, \( q \) is the electric charge, and \( G \) is the generation rate of electron-hole pairs by illumination. Open-circuit voltage of the cell is given by

\[
V_{oc} = \frac{kT}{q} \ln \left( \frac{I_L}{I_s} + 1 \right) \text{(2.14)}
\]

Where \( I_L \) is the light generated current and \( I_s \) is the diode saturation current. To get the maximum value of \( V_{oc} \), the \( I_s \) value must drop down to its minimum. The maximum of the current-voltage product along the curve leads to a maximum power output. The third factor that influences the efficiency is the fill factor (FF) of the cell. The higher the value of FF is the higher the efficiency of the cell is. Efficiency is given by:

\[
\eta = \frac{P_{out}}{P_{in}} = \frac{V_{oc} I_{sc}}{P_{in}} \times F.F \text{ (2.15)}
\]

Where,

\[
F.F = \frac{V_m I_m}{V_{oc} I_{sc}} \text{ (2.16)}
\]

Good fill factors can be obtained if the forward dark currents are low, series resistance is low, and shunt resistance is high. However, high band-gap materials give a high open circuit voltage and fill factor, while low band-gap materials yield higher photocurrents, leading to a maximum in the efficiency versus bandgap at about 1.5 ev [Hovel, 1975].
2.5.2. Photodegradation

If an a-Si:H solar cell is exposed to prolonged illumination at room temperature, a decrease in photoconductivity and an increase in dark conductivity, after the light soaking, is observed. This is due to the creation of additional localised gap states, as a result of bulk bond defects [Joannopoulos and Lucovsky 1984]. As an outcome the cells are degraded as they are exposed to sunlight. This effect was first discovered by Staebler and Wronski in [1977].

The bulk defects trap some of the photogenerated electrons, where they recombine. Consequently, these electrons do not participate in the output current and therefore some of this current is lost. It was reported that the effect was observed only in lightly doped films and an inverse effect has been noted in the undoped films, whereas heavily doped films did not show any effect [Street, 1991]. Various debates and interpretations have been reported when different techniques were used to study the effect and measure the gap states, among them photothermal deflection spectroscopy (PDS), electron spin resonance (ESR), and time-of-flight. However, one of the most considerable debates was whether the observed effect was due to the creation of new defects or the change in occupancy of existing states [Adler, 1978, Street, 1991].

The illumination time dependence of the number of dangling bonds is shown in figure 2.14.
Figure 2.14. The time dependent increase of the defect density by illumination of undoped a-Si:H [Stutzmann 1984, Street 1991].

It is obvious from the plot that the relation is definitely non-linear. However, when the defect density, $N_D$, is doubled, the initial value of $N_D$ increases as the cube root of time $\sqrt[3]{t}$, and hence is non-linear. No sign of saturation is observed in the figure 2.14 after the first few hours but the steady state is observed after longer illumination times or at higher light intensities. At higher elevated temperatures the steady state is obtained much faster for the same experimental conditions as indicated in figure 2.15.
Hence the dependence of the illumination intensity $G$ is also non-linear, having a power close to 0.6. The defect creation kinetics is therefore described by

$$N_D(t) = CG^{0.6}t^{0.33} \cdots \cdots \cdots (2.20)$$

, $C$ is a constant.

Furthermore, the defect density decreases with increase of temperature as may be seen in the same figure (figure 2.15). However, the inset plot shows insensitivity of the defect rate to the temperature.
2.4.3. Thickness And Optical Energy-Gap

The behaviour of a solar cell is affected in two ways if the thickness of the film is reduced. Firstly, the loss due to transmitted light increases, hence, the influence of the back contact becomes greater. Secondly, the dark current decreases due to excess recombination of the space charge carriers and dark injected carriers at the back surface of the sample. This is important when the minority carrier diffusion length is greater than the device's thickness. An accurate measure of the film thickness \(d\) and refractive index may be obtained over different wavelengths by measurement of interference patterns for transmittance.

![Diagram of transmitted light intensity T through an ideal film as a function of wavelength \(\lambda\).](image)

**Figure 2.16.** Predicted transmitted light intensity \(T\) through an ideal film as a function of wavelength \(\lambda\). [After Nakano et al., 1987, Cornish et al., 1992].

An example of spectrum is shown in figure 2.16. From this figure the peak maxima and minima are distinctive and the thickness of the film is given by

\[
d = \frac{1}{2n} \frac{\lambda_{\text{max}1} \cdot \lambda_{\text{max}2}}{\lambda_{\text{max}1} - \lambda_{\text{max}2}} \tag{2.21}
\]
Where; $n$ is the refractive index of the film, $\lambda_{\text{max}_1}$ and $\lambda_{\text{max}_2}$ are successive adjacent maxima of wavelengths as indicated in the figure 2.16. For two adjacent minimums in the figure (2.16), the $\lambda_{\text{max}}$ is changed to $\lambda_{\text{min}}$, and equation (2.21) may be re-written for adjacent maximum and minimum as below [Sakata et al., 1980].

$$d = \frac{1}{4n} \left( \frac{\lambda_{\text{max}} - \lambda_{\text{min}}}{\lambda_{\text{max}} - \lambda_{\text{min}}} \right) \quad (2.22)$$

Where $d$ is the thickness of the film, $n$ is refractive index for a-Si:H = 3.5.

$\lambda_{\text{max}}$ is local maxima on transmission curve

$\lambda_{\text{min}}$ is local minima on transmission curve.

The optical band-gap may be obtained from the absorption curve [Clare et al., 1988]. From the relation

$$I_x = I_z \exp(-\alpha x) \quad (2.23)$$

Where; $I_z$ is the initial intensity, $x$ is the depth of the material, $\alpha$ is the absorption coefficient at a given $\lambda$, and the experimentally determined values of $A = 1 - I_z/I_x$, the value of absorption coefficient ($\alpha$) can be calculated:

$$\alpha = \frac{\ln \log^{-1} A}{d} \quad (2.24)$$
The optical energy gap $E_{opt}$ may be determined from the plot of $\sqrt{\alpha h\nu}$ vs $E(ev)$ (Tauc plot) [Joannopoulos and Lucovsky, 1986] as indicated in figure 2.17.

**Figure 2.17.** The absorption coefficient plotted in the form suggested by Tauc et al [after Rahman, 1993].

Hence, $E_{opt}$ is determined from

$$\sqrt{\alpha h\nu} = c(h\nu - E_{opt}) \quad (2.25)$$
2.6. Techniques Applied To Characterisation Of a-Si:H

The carrier lifetime is one of the most important parameters in photovoltaic material because it determines solar cell characteristics. Transient illumination or forward bias produces free carriers, the recombination of minority carriers occurs with a characteristic time called minority carrier lifetime. This is the average time of the existence of an excess electron-hole pair. A variety of methods have been used to determine the carrier lifetime in hydrogenated amorphous silicon (a-Si:H) solar cells. Among them are time-of-flight, delayed field methods, photothermal displacement measurements, and carrier collection measurement as a function of wavelength and applied bias voltage [Sakata and Hayashi, 1990].

Vanmaekelbergh, van de Lagemaat and Schropp (1994) have used a technique related to impedance spectroscopy to study carrier generation in a-Si:H solar cells. The technique has shown that at low intensities the quantum yield (the number of charge carriers produced per photon) increases significantly above unity (Vanmaekelbergh, van de Lagemaat and Schropp, 1994). It has also been reported (Matsumura and Kasai 1995) that a similar effect exists at the other end of the spectral response, i.e. current carriers may be produced by the interaction of two sub-bandgap photons or/and transitions are produced by a single photon while the band-gap energy is reduced by extended band tails in the mobility gap. These two results have interesting theoretical and practical implications. Both mechanisms are fundamental properties of amorphous materials and are not found in crystalline materials. These techniques provide complementary information about the
production, transport (both drift and diffusion) and decay/recombination of the charge carriers. These parameters are related closely to the performance and stability of the cells.

The carrier lifetime depends on the level of dc bias illumination and the surface and interface of the sample affects trapping and recombination of the carriers in a-Si:H. Recombination takes place preferentially at trap sites such as dangling bonds. The number of dangling bonds in the band-gap is a measure of the quality of the photovoltaic material. Hence, the greater the concentration of dangling bonds, the faster the charge carrier recombination rate, and hence the shorter the minority carrier lifetime [Cornish, Subaer, Jennings, and Hefter, 1994]. Thus the minority carrier lifetime is an important parameter used to characterise and predict the performance of photovoltaic materials. Photo-induced open-circuit voltage decay is a variation of the open circuit voltage decay technique which was originally introduced by Gossiek [Mahan, 1979], and subsequently studied by several others. The core of the idea in this technique is to stimulate a light-sensitive semiconductor sample by a flash of light. From the results of this technique one may observe three regions which describe the minority carrier lifetime, as may be seen in figure 2.18.

I) The first region describes the high-level injection and the decay curve is linear and the minority carrier lifetime can be expressed as below:
\[ \tau = \frac{2kT}{q} \left| \frac{1}{dV_\infty / dt} \right| \quad \text{(2.17)} \]

Where \( k \): Boltzmann’s constant, \( T \): absolute temperature, \( q \): electron charge, and \( t \): time.

II) The second region describes an intermediate injection and the decay curve is again linear and \( \tau \) is expressed as:

\[ \tau = \frac{kT}{q} \left| \frac{1}{dV_\infty / dt} \right| \quad \text{(2.18)} \]

III) The last region of the decay curve is a low-injection and the Voc decay approaches an exponential time dependence[Mahan et al., 1979].

\[ V_\infty = \frac{kT}{q} \left[ \exp\left(\frac{qV(0)}{kT}\right) - 1 \right] \exp\left(\frac{-t}{T}\right) \quad \text{(2.19)} \]

\( V(0) \) is the open circuit voltage at the end of excitation. In the first region the excess minority carrier concentration exceeds the equilibrium majority carrier concentration. In region II the surplus minority carrier concentration is higher than the thermal-equilibrium majority carrier concentration. Finally, the third region is
low-injected and minority carrier concentration is lower than the equilibrium minority carrier concentration.

Figure 2.18. Theoretical curve of open circuit voltage [after Mahan et al., 1979].

2.6.1. Impedance Spectroscopy (IS) Measurements.

Impedance spectroscopy was first introduced in electrochemistry in 1960's. Since then it has been developed into a powerful and a practical tool for studying electrochemical problems in various systems during the last three decades [MacDonald, 1990]. Although there are pitfalls and critical issues associated with its
application, impedance spectroscopy has become a very important technique which has broadened the range of investigation of, for example, corrosion phenomena.

Impedance spectroscopy, (IS), has been used to study electrochemical cells in various areas such as electro-deposition, electro-organic synthesis, organic coating evaluation, batteries, and semiconductors. However, despite its importance, very limited attention has been paid to the application of this technique in the study of a-Si:H. The technique to be described is basically the same as the space charge spectroscopy (also referred to as admittance spectroscopy) method described by Lang [1982]. The analysis and interpretation of the results are owes its origins to the technique used in electrochemistry [Sluyters-Rehback and Sluyters, 1970]. There are other techniques currently used in investigating hydrogenated amorphous silicon solar cells which provide similar information. Between them capacitance-voltage (CV) measurements, transient photocurrent (TPC) [Weiczorek and Fuhs, 1989, Ulrichs et al., 1993], open circuit voltage decay (OCVD) [Mahan et al., 1979, Berry and Longrigg, 1988, Sakata and Hayashi 1990, Subaer 1995]. Furthermore, (IS) offers some distinct advantages over other comparative techniques used to characterise a-Si:H solar cells. These advantages include the small excitation potential amplitudes, easy to use, variation of presenting the data, and provide complementary information about the production, transport (drift and diffusion), trapping and decay/recombination of the charge carriers.
2.6.2. Transient Photocapacitance Spectroscopy.

There has been considerable interest in applying the transient photocapacitance spectroscopy (TPS) in the study of the deep defects in undoped hydrogenated amorphous silicon (a-Si:H) solar cells. The results from this technique have provided specific information about gap state dynamics and carrier transport processes [Gelatos and Cohen et. al., 1986, Lang et. al., 1982, and Kanicki et. al., 1989]. The technique, basically, appears qualitatively similar to optical absorption derived from photothermal deflection spectroscopy (PDS), except that the TPS method detects the net charge in the i-layer and is more sensitive. Like any other technique, TPS is relatively straightforward in interpreting the results, as it is not generally affected by the details of the transport processes. The experiments are carried out by detecting transitions within the depletion width with variation of d.c bias voltage.

The photocapacitance of a Schottky barrier increases substantially with light intensity and applied voltage, due to photogenerated holes captured by deep level traps in the depletion width. This phenomenon has been studied by deep level transient spectroscopy (DLTS) by Cohen and coworkers [Lang et al.1982]. The photocapacitance in a a-Si:H p-i-n solar cell is different from the Schottky barrier by the fact that the origin of photocapacitance is due to the displacement of mobile electrons and holes in response to an electric field. Furthermore, the DLTS studies of the p-i-n cell show that the trapped charge is insufficient to be the source of photocapacitance.
A) Creation of Photocapacitance

Illumination produces a large increase in the capacitance for high light intensity corresponding to AM1 solar radiation. This creates an electric field across the junction by displacing the space charge carriers to the contacts. As a result a lack of electrons near p-type and a lack of holes near n-type occurs. This mechanism creates photogenerated space charge carriers which are the source of photocapacitance as illustrated in figure 2.19.

![Diagram of p-i-n structure with photocapacitance](image)

**Figure 2.19.** Creation of photocapacitance by illumination [after Qi Wang and Crandall 1996].

The electric field in the depletion region is perturbed and increased by increasing the photogenerated carriers and increased further with high applied reverse bias voltage. As a consequence, the value of the photocapacitance gets higher and the carriers are further depleted to both sides. The photocapacitance signal is taken to be the
difference between the transient recorded in the light and in the dark, in other words; the capacitance in dark subtracted from the capacitance under illumination; i.e. 
\[ C_{ph} = C_{li} - C_{dk} \cdot \]

Qi Wang and Crandall [1996] have investigated the collapse of the electric field by using this technique and they used the photocapacitance as a measure to probe the collapse field. Crandall [1982] has described the photocapacitance associated with photogenerated space charge carriers as a measure of the drift mobility of electrons and holes.

Typically, photocapacitance \( C_{ph} \) is a difference between the capacitance under illumination, \( C_{li} \), and in the dark, \( C_{dk} \), as defined earlier. However, any space charge has an associated capacitance [ Qi Wang and Crandell, 1996]. The space charge in the i-layer is given by:

\[
Q = \frac{1}{2} \frac{eG L^2}{\mu E} \quad (2.20)
\]

Where \( e \) is the magnitude of the electric charge, \( G \) is the generation rate of electron-hole pairs, \( L \) the i-layer thickness, \( E \) is the electric field in i-layer, and \( \mu \) is the charge mobility. Equation 2.20 due to the holes in the i-layer becomes:

\[
Q_h = \frac{1}{2} \frac{eG L^2}{\mu_h E} \quad (2.21)
\]
and due to the electrons in the i-layer.

\[ Q_e = \frac{1}{2} eGL^2 \frac{1}{\mu_e E} \quad (2.22) \]

These electron and hole space charges in the i-layer induce opposite charges on the contacts by induction, which can be detected by capacitance measurement. The charge carrier capacitance is given in terms of change of charge with voltage.

\[ C = \frac{\partial Q}{\partial V} \Rightarrow C = \frac{1}{2} eGL^3 \frac{1}{\mu V^2} \quad (2.23) \]

The capacitance for electron and hole in the i-layer is given by:

\[ C_e = \frac{1}{2} eGL^3 \frac{1}{\mu_e V^2} \quad (2.24) \]

\[ C_h = \frac{1}{2} eGL^3 \frac{1}{\mu_h V^2} \quad (2.25) \]

Since electron charge \( Q_e \) and hole charge \( Q_h \) induce negative and positive charges in the n and p layers respectively, and photocapacitance must be the sum of electron capacitance and hole capacitance in series.

\[ C_{ph} = \frac{eGL^3}{2V^2} (\mu_e + \mu_h) \quad (2.26) \]

\[ C_{ph} = \frac{E^2 I_s}{2V^2 (\mu_e + \mu_h)} \quad (2.27) \]
B) Effect of applied bias voltage

Figure 2.20 shows the effect of reverse bias voltages on photogenerated space charge carriers. The values of photocapacitance are significantly increased with increasing applied bias voltage. A large change of Photocapacitance was occurred with increasing the forward bias voltage whereas a much smaller change is observed for the same change of reverse bias voltage. The forward bias photocapacitance is higher than its value in reverse bias, and the consequence is a decrease in impedance.

Figure 2.20. A typical voltage dependence of photocapacitance in p-i-n a-Si:H solar cells [after Qi Wang and Crandell, 1996].
Impedance of a circuit consisting of a resistor and capacitor is given by

\[ Z = \sqrt{R^2 + X_c^2} \]

Where \( X_c \) is capacitance inductance. The capacitance inductance is defined as

\[ X_c = \frac{1}{2\pi fC} \]

However, at zero electric field the photogenerated charge carriers are sustained, electrons and holes balance at all points. As electric field increases electrons and holes drift according to the direction of the field, i.e. electrons to n side and holes to p side, as a result the number of negative carriers in the p-layer and positive carriers in the n-layer reduces. The significant increase in the values of photocapacitance with bias voltage is attributed to the increase in the electric field which was enhanced by the reverse bias voltage.

The transition processes in a-Si:H using TPS may be described by three mechanisms categorised according to excitation energies which are: a) \( D^- \rightarrow D^+ + e \), b) \( D^+ \rightarrow D^+ + e \), c) \( D^+ \rightarrow D^- + h \) Where \( D^-, D^+, \) and \( D^+ \) denote the three charge states of the dominant deep defects. These mechanisms are illustrated in figure 2.21.
For the energy system below the mid-gap, there is only excitation of trapped gap state electrons to the conduction band contributing to the photocapacitance signal. Whereas for excitation energy above the mid-gap, however, all types of transitions are possible. Finally, the results of transient photocapacitance measurements could lead to a considerable information in the study of undoped a-Si:H solar cells, particularly, for studies of light-induced changes in this material.
2.6.3. Sub-bandgap Energy Interactions

Infrared stimulated current in intrinsic a-Si:H solar cells has been studied over a decade ago by Wu and co-workers [1986]. The overshoot of the IR photocurrent was observed before a steady state was reached. This overshoot was interpreted in terms of a model so called two-step excitations [Xu Zheng-Yi et al., 1987]. The model basically, involves the mobility carriers (electrons) from the extended states of the valence band and occupied gap states. Based on the assumption that \( h\nu \) of red and IR radiations are less than the band gap, charge transitions are possible by multiple photon excitations. However, electrons in the valence band edge \( E_v \) may be simultaneously excited to the unoccupied gap states; and during the next excitation event an occupied electron from the upper level of the gap states reaches the empty conduction band edges. Thereby, sub-bandgap photon interactions ultimately contribute to the primary photocurrent that is detected in the output circuit [Zhou et al., 1991]. Following the approach of Xu Zheng et al., [1987] the rate equations determining the density of excess free carriers \( n(t) \) and the occupancy function \( f(E,t) \) are as follows:

\[
\frac{dn(t)}{dt} = \int_{E_v}^{E_c} \left\{ v(E) f(E,t) - b n(t)(1 - f(E,t)) \right\} g(E) dE
\]

\[
+ b \int_{E_v - h\nu}^{E_v} f(E,t) g(E) dE - n(t) / \tau
\]

and
\[
\frac{df(E,t)}{dt} = b_n(t)(1 - f(E,t)) - v(E)f(E,t)b_\theta(E - E_c + h\nu)f(E,t) \\
+ b\theta'(E_v + h\nu - E)(1 - f(E,t))
\]

Where \(v(E)\) is thermal emission rate, \(g(E)\) is density of recombination centres, \(b_i\) is the capture rate. The term \(n(t)/\tau\) corresponds to the contribution of recombination, \(\tau\) is the average recombination time. The terms associated with \(b\) and \(b'\) express the contributions to the release rate arising from the first and the second excitation step, respectively. \(\theta(x)\) stands for a step function defined as \(\theta(x)=1\) for \(x > 0\), \(\theta(x) = 0\) otherwise, when \(x = (E - E_c + h\nu)\) and \(x = (E - E_v + h\nu)\) for \(\theta'(x)\).

The above authors have considered the amphoteric nature of the band defect centre before explaining sub-bandgap transitions in a-Si:H solar cells. Each dangling bond centre can have three states of occupancy, empty \((D^+)\), singly \((D^+)\), or doubly \((D^-)\) occupied [Gelatas and Cohen 1986, J. D. Cohen 1987, D. Vanmaekelbergh and J. van de Lagemaat 1994]. A doubly occupied dangling bond can capture a hole and become neutral. From a single occupied state dangling bond, an electron can be thermally emitted to the conduction band, creating an empty occupied state. An empty state can be converted to doubly occupied by emitting two holes thermally into the valence band, hence an extra electron/hole pair is detected in the external circuit [Zhou et al. 1991].

To investigate the quantum efficiency of an a-Si:H solar cell, they have taken the generation of multiple photon electron/hole pairs into consideration as well as the single photon. Amorphous silicon does not have a clearly defined band structure and
behaves much like a direct semiconductor since the conservation of momentum is not required. Hence, photons are absorbed over a wide range of illumination spectra. Although the IR and red photon energies (hv) are less than the band gap, it is possible to excite electrons from the valence band to the conduction band by a single photon or by multiple photons as illustrated in figure 2.22. This opens up the possibility of creating electron/hole pairs by sub-bandgap photon absorption.

The effective correlation energy \( U_{\text{eff}} \) that separates the upper level of the gap states is as small as 0.3-0.4ev [Zhou et al., 1991]. Hence, the space charge carriers that are located near these states only require a few tenths of an electronvolt to transfer to the conduction band where they recombine and are collected usefully. However, red and infra-red light photons, used in this project, were found to create electron/hole pairs that are sufficient to contribute in the primary photocurrent. Thereby, the increase in quantum efficiency of the cell may be observed.

The above authors have explained the over shoot of photocurrent under infrared illumination in two steps. Firstly, electrons might be excited by sub-bandgap energy (hv) from occupied gap states to states above the conduction band edge Ec. Second step, electrons may be simultaneously excited from the extended states below the valence band edge Ev to empty localised gap states. As a result of energy conservation, only electrons situated in gap states above Ec - hv can be excited into extended states above Ec, and only empty states below Ev + hv can gain electrons via the second excitation step.
Figure 2.22. Schematic diagram illustrates the two step transitions by sub-bandgap energy.
CHAPTER 3

The Impedance Spectroscopy (IS) Technique

3.1 Introduction

Only a relatively brief background on impedance spectroscopy (IS) technique has been presented in physics so far, particularly in the study of hydrogenated amorphous silicon solar cells. In IS, one deals not just with impedance but with a few more closely related functions which can be sub-combined under the nomination of “Immitances”. Thus the IS can also stand for immitance spectroscopy. The other functions are: Impedance $Z = Z' - jZ''$, Admittance $Y = Z^{-1}$, Complex dielectric constant $\varepsilon = \varepsilon' - j\varepsilon''$, and complex modulus; $M = \varepsilon^{-1}$. Where j=√-1 [Brug et al., 1984].

The technique of impedance spectroscopy (IS) is widely used in electrochemistry to investigate processes that proceed at different rates by varying the modulation frequency, fast and slow processes may be identified. Results may be interpreted by modeling the electrochemical cell as an equivalent circuit [Sluyters-Rehbach and Sluyters, 1970].

The ideal case, which allows estimation of the values of microscopic quantities which characterise the solar cell device in adequate way, is to analyse the data by fitting them to a detailed microscopic model of the system. One which yields an explicit form or definite expression for impedance as a function of frequency, and affect of bias voltage on the parameters of the equivalent circuit of the cell. The
simplest model to start with, consists of an equivalent electrical circuit composed of elements such as capacitors and resistors. For the characterisation of a-Si:H solar cells, the physical interest concentrates on two basic elements which always appear in modeling the system, capacitance (diffusion and transition) and resistance (dynamic and parallel). These parameters are the key bulk and surface response and extensive quantities of the system.

The technique to be described is basically the same as the space charge spectroscopy method (also referred to as admittance spectroscopy) described by Cohen and co-workers (1982); however, the analysis and interpretation of the results owe their origins to the technique used in electrochemistry.

The physical model of the system mechanisms was found to fit the experimental data much better than those for other techniques that have been used to model p-i-n a-Si:H solar cells [Suresh, 1995], [Pellegrino et al., 1997], [Meren et al., 1997]. The main advantage of the present technique over the others is that the results may be presented in various ways, $Z'\times Z''$, $Z'Z''$ vs log f, $\Phi$ vs log f, and $ZvV_b$, [MacDonald, 1987], [MacDonald et al., 1991], [Brug et al., 1984], and [Bruin and Franklin, 1981] which confirm the validity of the results.
3.2 Fundamentals Aspects of Impedance Spectroscopy (IS).

A number of reviews have discussed the theory of impedance spectroscopy in electrochemistry and its application in solid semiconductor studies among them MacDonald [1990]. These reviews suggest that two main areas of application are rapid estimates of a wide range of optical absorption of solid semiconductors, and practical insight into microscopic mechanism of minority carrier charges.

The power of IS lies in the fact that it is essentially a steady-state technique that is capable of accessing relaxation phenomena whose relaxation times vary over many orders in magnitude. The steady-state character permits the use of signal averaging methods within a single experiment to gain the desired level of precision, and the wide range of frequency ($10^{-4} - 10^6$) permits a wide range of interfacial processes to be investigated, and hence allow the cell to be modelled as an equivalent circuit and determine its parameters which are crucial for performance of the cell.

The theoretical definition of impedance is important for understanding the power and limitations of the technique.

$$Z(f) = \frac{V(f)}{I(f)}$$

$f$ is the frequency, $V$ and $I$ are the voltage and current respectively.

$$f = \frac{\omega}{2\pi}$$
In terms of the steady-state sinusoidal frequency domain, the transfer function becomes:

\[
Z(j\omega) = \frac{F[V(t)]}{F[I(t)]} = \frac{V(j\omega)}{I(j\omega)}
\]

Where \( F \) signifies the Fourier transform, \( V(j\omega) \), and \( I(j\omega) \) are the sinusoidal voltage and current respectively, \( Z(j\omega) \) is the impedance of the circuit [Sluyters-Rehbach and Sluyters 1970, Beach and Justice 1986].

From the theoretical point of view, the impedance is one of the most important quantities that can be measured. This is because, it can be used over wide range of frequencies. In practice, although IS measurements are applied over a limited range of frequencies, they still provides significant information about the system. Impedance is commonly written in the form \( Z(j\omega) = Z' - jZ'' \) where \( j = \sqrt{-1} \), \( Z' \), \( Z'' \) are the real and imaginary parts of the impedance respectively. Both parts are real numbers, which are related to the magnitude of impedance and the phase angle by:

\[
|Z(j\omega)| = \sqrt{(Z')^2 + (Z'')^2}
\]

\[
\tan \Phi = \frac{Z''}{Z'}, \quad \text{Where } \Phi \text{ is the phase angle.}
\]

This can be rewritten as:

\[
Z(j\omega) = |Z|e^{j\phi}
\]
These two mathematical forms lead directly to the two common methods displaying the impedance data: (Z' vs Z') and (Z' vs log f and Z'' vs log f), Nyquist or so called Cole-Cole, and Bode plots respectively [Pinkowski, Juttner, and Lorenz, 1990]. In this project both plots will be used to present the data, since each form offers specific advantages of interpretation of the data in certain situations. The first Nyquist plot is adequate for carrier mechanistic analysis because the number of relaxations and their mechanistic implications are often more apparent. The Bode form employ frequency directly as the independent variable, hence more precise comparison between experimental and calculated impedance spectra can be made.

![Nyquist plot](image)

**Figure 3.1.** Imaginary part of impedance as a function of real part in complex plane (Nyquist or Cole-Cole).
3.2. Imaginary and real parts of impedance as a function of frequency (Bode plot).

3.3. Equivalent Circuit Analysis of an Ideal System

Figure 3.3 shows a response of the impedance of the equivalent circuit with modulation frequency for an ideal electrochemical cell.

Figure 3.3. Complex impedance plane curve [after Sluyters et al., 1970].
The semicircular curve in the figure is obtained where the imaginary part of impedance plotted as a function of real part in the complex plane.

At \( \omega \to \infty \), \( Z_{\text{imaginary}} \to 0 \) and the intercept on the X-axis gives the series resistance, \( (R_\Omega) \). At \( \omega \to 0 \), again \( Z_{\text{imaginary}} \to 0 \) and the intercept of the right hand side on the X-axis gives the sum of \( R_\Omega \) and shunt resistance, \( R_\phi \), i.e. \( (R_\Omega + R_\phi) \).

Thus, the diameter of the semicircle is equal to \( R_\phi \).

It can be noticed from the figure (3.3) that the plot is very nearly semicircular in shape indicating that the AC equivalent circuit of the cell consists of a shunt resistance \( R_\phi \) and \( C \) in parallel connected to a series resistance \( R_\Omega \), as shown in figure 3.4a.

Figure 3.4. a) Equivalent circuit diagram of ideal electrochemical cell, b) Reduced series resistance of equivalent circuit of the ideal cell.
This simple circuit (figure 3.4a) can be employed to describe the impedance characteristics and may be reduced to a resistor and capacitor in parallel at zero frequency [MacDonald, 1987] as shown in figure 3.4b. Following the approach of Sluyters-Rehback and Sluyters [1970] the impedance for this simple equivalent circuit is given by:

\[
Z = R_\alpha + \frac{R_\Theta}{1 + j\omega C_{dl} R_\Theta}
\]

or

\[
Z = Z' - jZ''
\]

Where:

\[
Z' = R_\alpha + \frac{R_\Theta + \sigma \omega^{-\frac{1}{2}}}{\left(\sigma \omega^{\frac{1}{2}} C_{dl} + 1\right)^2 + \omega^2 C_{dl} \left(R_\Theta + \sigma \omega^{-\frac{1}{2}}\right)^2}
\]

\[
Z'' = -\frac{\omega C_{dl} \left(R_\Theta + \sigma \omega^{-\frac{1}{2}}\right)^2 + \sigma^2 C_{dl} + \sigma \omega^{-\frac{1}{2}}}{\left(\sigma \omega^{\frac{1}{2}} C_{dl} + 1\right)^2 + \omega^2 C_{dl} \left(R_\Theta + \sigma \omega^{-\frac{1}{2}}\right)^2}
\]

Where \(\sigma\) is the conductivity of the system. At sufficiently high frequencies the value of \(\sigma \omega^{-\frac{1}{2}}\) is very small compare to \(R_\Theta\) and can be neglected. Hence, the equations above become as follow:

\[
Z' = R_\alpha + \frac{R_\Theta}{1 + \omega^2 C_{dl} R_\Theta^2}
\]

\[
Z'' = \frac{\omega C_{dl} R_\Theta^2}{1 + \omega^2 C_{dl} R_\Theta^2}
\]
The values of $\omega$ and $C_{dl}$ are given as

$$\omega = \frac{Z''}{(Z - R_\Omega)R_\Theta C_{dl}} \quad , \quad C_{dl} = \sqrt{\frac{R_\Theta - Z'}{\omega^2 Z'R_\Theta^2}}$$

Where $\omega$ is an angular frequency and equal to $2\pi f$, $C_{dl}$ is double layer capacitance, $R_\Omega$ is series resistance, and $R_\Theta$ is the shunt resistance of the cell. The most elegant way of describing a complex plan plot is to find algebraic equation by eliminating the variable (frequency in this case) in the equations between $Z'$ and $Z''$. Since, the complex plot has the shape of semicircle, then $Z'$ and $Z''$ may be written as below

$$\left(Z' - R_\Omega - \frac{R_\Theta}{2}\right)^2 + (Z'')^2 = \left(\frac{R_\Theta}{2}\right)^2$$

The structure of amorphous silicon (a-Si:H) solar cell has similarities to the model of the layers at an electrolyte/electrode interface. It is also apparent from other techniques that within the a-Si:H photovoltaic cell there are a number of processes that proceed at different rates. The results allow us to distinguish the processes that proceed on different time scales, determine the parameters of equivalent circuit of the cell, and describe its performance. However, the results have demonstrated that the impedance spectroscopy can be carried out at different bias voltages which is equivalent to making measurements on different point on the IV characteristic curve.
Figure 3.5. The I-V characteristic curve for a-Si:H p-i-n solar cell.

The series and shunt resistances may be obtained from the slope of the IV characteristics for a-Si:H p-i-n solar cell illuminated by AM1.5 global irradiance and is given by $R = \frac{\Delta V}{\Delta I}$, this yields $R_{sh}$ at $V = 0$ and $R_s$ at $V = V_{oc}$.

Where $\Delta V$ is the change in the bias voltage and $\Delta I$ is the change in the current density. Hence, any change in the applied bias voltage would change the cell’s parameters and may lead to valuable information on the density of states, generation of electron/hole, and minority carrier lifetime. The general expression of complex impedance is given by

$$Z = Z' - iZ''$$
\[ Z' = |Z| \cos \Phi \]
\[ Z'' = |Z| \sin \Phi \]

Where \( \Phi \) is the phase shift, and \( Z' \) and \( Z'' \) are real and imaginary part of impedances respectively and \( i = \sqrt{-1} \). The relation between sine wave current and voltage is entirely described by two quantities, namely, the ratio of the amplitudes, 
\[ |Z| = \frac{V_m}{I_m} \], and the phase shift \( \Phi \) between current and voltage [Sluyters-Rehbach and Sluyters 1970]. The AC equivalent circuit of this solar cell consists of a resistor and a capacitor in parallel as shown in figure 3.6a. The diagram in (a) may formally be reduced to a simpler circuit of only two parameters [Beach and Justice 1986] consisting of a shunt resistor and a capacitor in parallel as shown in (b).

![Diagram of AC equivalent circuit](image)

**Figure 3.6.** Shows the general form of AC equivalent circuit used in the analysis of the a-Si:H photovoltaic cells. a) At a given frequency, b) at zero frequency.

C is the sum of \( (C_T) \) transition capacitance (dominant in illuminated cell) and \( (C_d) \) diffusion capacitance (dominant in dark cell). \( R_{sh} \) is the shunt resistance of the cell.
which is the resultant of \( R_d \) (dynamic resistance) and \( R_p \) (parallel resistance), \( R_s \) is series resistance due to bulk and interconnects, \( I_{sc} \) is short circuit current of the cell.

The series resistance is due to the bulk carrier interactions and the metallic contacts in the interconnection regions. The dynamic resistance is due to leakage across the depletion region and parallel resistance is caused by recombination in the junction region. These parameters directly influence the solar cell behaviour; hence, calculation of their values is crucial to obtain information about microscopic mechanisms of the cell. Since the \( C \) and \( R_{sh} \) in parallel, then the equivalent circuit has a single time constant given by:

\[
\tau = R_{sh} \times \frac{C}{2}, \quad R_{sh} = \frac{R_p \times R_d}{R_p + R_d}, \quad C = C_T + C_d
\]

The values of \((C_T + C_d)\) can experimentally be determined from the resonance \( \omega_{max} \) at maximum value of \((Z'')\) imaginary part of the impedance i.e.

\[
C = \frac{1}{\omega Z'_{max}} \quad Z'' = \frac{1}{2\pi f C} \Rightarrow C = \frac{1}{2\pi f Z''_{max}} \quad [\text{Suresh, 1995}]
\]

When \( Z'' \) is the imaginary part of impedance and shunt resistance may be obtained from:

\[
R_{sh} = \frac{(Z' - R_s)^2 \pm (Z'')^2}{(Z' - R_s)} \quad [\text{Sluyters-Rehback and Sluyters, 1970}].
\]

\( Z' \) is the real part of impedance at maximum imaginary part \((Z''_{max})\). From the characteristic semicircular plots (imaginary part of impedance as a function of real
part), series resistance, dynamic resistance, diffusion capacitance, transition capacitance, and minority carrier lifetime can be calculated. The results showed that the dynamic resistance is extremely sensitive to light soaking and its values decrease significantly with increasing the light, whereas the series resistance has not been affected by the light [Merten et al., 1997].

![Graphs showing impedance spectrum](image)

**Figure 3.7.** Impedance spectrum of p-i-n a-Si:H solar cell at different bias voltages [after Suresh, 1995].
The values of dynamic resistance and capacitance have also been affected by the temperature change and bias voltage [Kohei Uosaki et al. 1990], [Richard P. Buck, 1987], and [M. Stieble and K. Juttener 1990] as we describe these effects later in this chapter.

If the capacitance and the shunt resistance are constant with the modulation frequency then the impedance spectrum of such a circuit is a semicircle as in figure 3.7 a&b. If C and R or either of them varies with modulation frequency then the impedance spectrum deviates from a semicircle tending towards a straight line as indicated in figure 3.7c.

3.4. The Interpretation of IS in a-Si:H

Impedance spectroscopy (IS) is used to study hydrogenated amorphous silicon solar cells to investigate the type of processes in the bulk and interface of the sample using modulation of voltage over a range of frequency. Interpretation of the plots which are obtainable from the experimental data lead us to gain valuable information about transport mechanism of minority carriers in the bulk and interface of the sample and hence, predict its performance. Furthermore, minority carrier lifetime and conductivity of the cell can be calculated from the result. However, the interpretation of experimental impedance spectroscopy data is not as easy as we imagine. In fact, the technique is often not fully used due to the difficulties in developing suitable models for simulating the impedance behaviour and in developing fitting programs.
for analysing the data [de Bruin and Franklin, 1981, Brug et al., 1984, MacDonald, 1987, Stieble and Juttner, 1990].

3.5. Practical Measurements

In practice, the impedance spectra observed in a-Si:H solar cells experimentally often deviate from the ideal behaviour and often cause confusion as to its correct interpretation. Usually this deviation results in a flattened semicircle or tending towards a straight line. A typical impedance result which shows this deviation from the ideal behaviour is shown in figure 3.8.

![Figure 3.8. Deviation from the ideal behaviour of the impedance curve.](image-url)
These flattened semicircle curves are commonly observed but are not easily explained [MacDonald, 1987]. A frequent interpretation for that is based on the assumption that the elements of the equivalent circuit are frequency dependent in the low frequency region where the bulk effects dominate the mechanism, i.e. take values as a function of frequency. Nevertheless, in electrochemistry various debates and interpretations have been reported about depressed and flattened semicircles; and they also suggested a careful analysis of (IS) is critical for correctly interpreting impedance data in every individual system [Uosaki, Okazaki, and Kita, 1990].

3.6 Effect of Applied Bias Voltage

Figure 3.9 shows a Cole-Cole plot [Buch 1987, Uosaki, Okazaki, and Kita 1990, Stieble and Juttner 1990] in which the imaginary part of impedance is plotted against the real part of the impedance for electrochemical cell at 256K for various bias voltages. The effect of applied dc voltage on impedance and the parameters of the equivalent circuit was probed experimentally by many groups. Figure 3.9 shows that the shunt resistance decreases with increasing the applied bias voltage. In fact, the value of $R_\text{sh}$ starts to decrease significantly when the bias exceeds 1.6v, whereas the series resistance, $R_\alpha$, has not been affected. The effect of the bias voltage is even much more apparent in terms of the shape of the curves. The semicircular shape of the curve at 1.8V is starting to become apparent, though it is not evident at lower
volatges. At lower bias voltages a large change in the imaginary part of impedance accompanied by a small change in the real part at a given frequency, resulted in a straight line. This is illustrated in more detail in chapter 5. The values of series resistance may be obtained from the interception of imaginary part of impedance at very high frequency, with X-axis. The conductivity of the system could be calculated from the thickness of the sample and value of series resistance.

\[ \sigma = \frac{1}{R_{ts} d} \]  

[MacDonald, 1990]

d is the thickness of the sample.

Temperature of the sample is another parameter that affects the impedance and equivalent circuit elements. However, both shunt and series resistances are high at low temperature compared to their values at higher temperatures reflecting the slow transport of the carriers at low temperature. However, the temperature scale is isomorphic to a logarithmic frequency [Lang et al., 1982]. Hence, making measurements with modulation frequency provides similar information to those obtained by temperature variations, if the dynamics are controlled by a thermally activated variable such as thermal detrapping rate as we will mention in more detail in the final two chapters.
Figure 3.9. Effect of applied reverse bias voltage on impedance of the cell [Kohei Uosaki et al., 1990].

3.7. Circuits and Models

In chemistry, the two types of reaction conditions which often occur are supported and unsupported reactions. These reactions are strongly related to the mobility of the
charged carriers in the solution. However, supported reactions generally occur in liquid electrolytes, where both positive and negative species are mobile, usually without a large difference in mobilities [MacDonald, 1987]. The reactions in supported electrode decouple the charged ionic species of interest from the rest of the charges in the system. Thus, electrical effects are very much easier to calculate in an approximate but usually adequately accurate way. Unsupported reactions, however, normally happen in solids with electronic conduction such as semiconductors, where the difference in charged carriers is relatively high. The situation is quite different here, where Poisson’s equation couples both positively and negatively charged carriers together strongly. It is, therefore, much more difficult to solve electrical response problems. In the study of hydrogenated amorphous silicon (a-Si:H) solar cells although charges of both signs may be mobile, it is common to encounter situations where the difference in mobility is so large that the slower charges may be taken as completely immobile over the time scale of the experiment. Hence, the decoupling of charged carriers in the depletion region required a large potential difference across the cell but not higher than the thermal voltage \[ V_T = \frac{kT}{e}. \]

The presence of a potential difference sometimes complicates the analysis of the results greatly. However, the p.d drives the mobile carriers (electrons) towards the n-side and accumulates the positive charges at the p-side preventing further recombinations in the depletion region of the p-i-n solar cells, as was illustrated in section 2.6.2.
When an equivalent circuit involves only ideal elements, it is found that some circuits with same number of elements but with different interconnection may yield exactly the same impedance for all frequencies [Fraceschetti et al 1991]. Figure 3.10 shows three such circuits: a) is a series type, b) essentially parallel, and c) is a hierarchical connection. The circuit elements must have different values in order to have the same impedance in all circuits. This is why the circuit elements are named differently [MacDonald, 1987]. The circuits in figure 3.10 represent equivalent circuits of module cells made from three films. Each film can be modelled into a simple equivalent circuit consist of resistor in parallel with a capacitor connected to a series resistor as was shown earlier in figure 3.7a.

In the study of p-i-n solar cells, there is prior usage in defining $R_d$ as dynamic resistance of space charge carriers in the depletion region, $R_{sh}$ as a general definition of the resistance due to recombination in the transition region, and $R_{series}$ is used as a series resistance due to bulk and interconnections. In equivalent circuits of electrochemical cells, the quantity $C$ appears defined as just the double-layer capacitance and written as $C_{dl}$ without distinction being made between illumination and dark concepts. In the study of a-Si:H solar cells, $C_{dl}$ is used for the dark cell and $C_T$ for the illuminated. As mentioned earlier, one or more elements in the equivalent circuit might be frequency dependent in the low frequency region, where bulk effects dominate. This frequency dependence could lead to deviation of the curve from its semicircular shape.

80
a) A series type.

![Series Type Circuit Diagram](image)

b) Maxwell type.

![Maxwell Type Circuit Diagram](image)

c) Ladder type.

![Ladder Type Circuit Diagram](image)

Figure 3.10. Three circuits which can have exactly the same impedance-frequency relation [MacDonald, 1987].
CHAPTER 4

EXPERIMENTAL

4.1 Sample Preparation.

4.1.1 Glow-Discharge (CVD) or (PECVD):

Plasma enhanced chemical vapour decomposition usually referred to as glow discharge (GD), is the method which was used for sample preparation in this study. A photograph of the system is shown in figure 4.1. The system was planned to produce a-Si:H by GD; (PECVD), and to be able to move the sample under vacuum to remote UHV analysis chambers elsewhere [Lund, 1993]. The following describes the main parts in this system briefly:

a) Main Chamber.

The main chamber which is cylindrical in shape with a diameter of 200mm and 200mm high was constructed at Murdoch University. This chamber is shown in figure 4.2. Ports are provided to allow connection to pumping and gas inlet systems, insertion and removal of substrates, windows, gauges, substrate heating, radio-frequency (RF) power, and some other facilities. The system is constructed from stainless steel, argon arc-welded with demountable joints using either standard NW or KF seals with viton 'O' rings or FC flanges with viton or copper gaskets [Cornish, Jennings, Hefter, 1992].
Figure 4.1. Photograph of Murdoch University glow discharge deposition system used for preparing the samples.
b) Pumping System.

Figure 4.3 shows a schematic diagram of the gas handling system. This vacuum system contains two rotary pumps and an oil-filled diffusion pump. A single stage rotary pump is used to remove air from the system when evacuating from atmosphere. The sealed two stage rotary pump was used for pumping silane and was not exposed to air. While this pump is not in use it is back-filled with an inert gas to prevent reactions between oxygen ($O_2$) and any silane($SiH_4$) dissolved in the oil [Lund, 1993].
c) Gas Inlet.

In operation, the gas regulators are purged of air or other contaminant gases using argon, in the case of silane, diborane and phosphine, or by flushing for other gases. The regulators are all of the high purity type and are evacuable with several purge/evacuation cycles being used to minimise contamination of the source gases. Gas flow to the chamber is electronically controlled by mass flowmeters which have been set to allow up to five gases to be mixed in predetermined proportions in the manifold prior to admission to the main chamber. Following the deposition, gases remaining in the system are diverted to the rotary pump via a separate manifold and the gas handling system is evacuated and purged to remove traces of silane and other reactive or toxic gases.

d) Deposition System and Related Elements

The substrate holder and radio-frequency power supply system are the main parts in this region. The substrate holder has been designed to employ either of two alternative specimen mounting techniques. In the early stages of the system's operation, the substrate holder and heating block were designed to allow preparation of films on various types and sizes of substrates. Figure 4.4 shows the substrate heating block on which the substrates are placed directly. However, in an alternative configuration, the block was inverted and a sample mask was used to hold the substrates in position.
Figure 4.3. The vacuum and the gas supply system of Murdoch glow discharge system [after Cornish et al., 1992].
4.2 Deposition Process

4.2.1 Glow Discharge Deposition Parameters in a-Si:H

To obtain a high quality of a-Si:H film by the glow discharge method one must control the primary deposition parameters which are: power density, substrate temperature, gas pressure, feed-gas concentration, and flow rate.

![Diagram](https://example.com/diagram)

Figure 4.4. Deposition region and substrate holder.

a) Power Density

In glow discharge, the deposition rate increases monotonically with radio frequency (RF) power density until it is limited by the gas flow rate. This increase of deposition rate by increasing RF, however, results in damage to the film, hence the resulting film is of poor quality. Therefore, controlling power density is important.
b) Substrate Temperature

The deposition temperature is the most influential parameter since it controls the chemical reactions on the growing surface [Street, 1991]. During a-Si:H deposition, the substrate temperature affects the hydrogen elimination and the reconstruction of atoms after the deposition precursors, such as $SiH_x$, have arrived on the growing film surface. The optimum deposition temperature varies between 200-300°C.

c) Gas Pressure.

The deposition rate is proportional to the pressure. Gas pressure determines the mean free path for collision of gas molecules. For high quality film deposition a pressure as high as 0.5 torr is favoured.

d) Gas Flow Rate

The gas flow rate is another important primary deposition parameter. The flow rate is inversely related to residence time, the average time that a gas molecule spends in the plasma. This time determines the probability that the molecule will be dissociated and incorporated into the growing film. The longer the residence time, the greater the depletion of the feed stock gas [Luft and Tsuo, 1993]. This depletion is a crucial parameter affecting film quality.

In this study all samples were fabricated at a substrate temperature of 225°C, with pure silane as starting gas material, gas pressure in the range 0.1-0.5 torr, the radio frequency power was between 2-4 watt. The glow discharge plasma was produced by applying an RF voltage at a frequency at 13.56MHz via an impedance-matching
at 13.56MHz via an impedance-matching circuit between the substrate holder and the stainless steel RF electrode. The plasma was sustained by the RF electric field.

4.2.2. Aluminum Deposition.

Although the technique was applied on numbers of samples, the results of two samples are presented in this study. The p-i-n a-Si:H solar cells used in this work were made on commercially prepared, 100 nm thick, untextured TCO on glass substrate. A-Si:H films were deposited by plasma enhanced chemical vapour decomposition (PECVD) at a substrate temperature of 225°C. The p-layer was deposited, on the top of the TCO, from a mixture of the starting gas materials (pure silane $SiH_4$) and 1% diborane in argon, the i-layer (0.4μm thick) from pure silane and the n-layer from a mixture of pure silane and 1% phosphine in argon. The silane gas flow into the evacuated chamber was controlled by a valve and the gas pressure was controlled by changing the flow- conductance. The silane gas was admitted into the evacuated reaction chamber at a controlled flow rate and pressure. The influential parameters which determine the structure and photoelectric properties in plasma enhanced chemical vapour decomposition process are the starting gas ($SiH_4$), gas flow rate, gas pressure, power-source frequency, d.c bias voltage and substrate temperature. Contact to the n-layer was provided by evaporating pure aluminum spots of (2.4 and 5mm) in diameters. The deposition of the aluminum contact on the a-Si:H device has been described elsewhere by Subaer [1995]. The evaporation system for depositing Al contacts on the film surface is shown in figure 4.5.
The system is evacuated by a two stage rotary pump and an oil-filled diffusion pump. The vacuum system was pumped down for several hours to obtain a pressure of \( \leq 10^{-5} \) torr before the deposition process was conducted. Pure aluminum wire was wound on a 0.20mm diameter tungsten filament and the current to heat the filament and evaporate the aluminum was 25 amperes. The substrate with the a-Si:H film was put above the filament overturned on the top of a metal mask. The original mask was made to evaporate 40 similar spots about 2.4 mm in diameter with separation distance of 0.1 mm between each two spots. The new mask was made with 10 identical spots, 5 mm in diameters and 2.5 mm separation distance. These larger spots have been tested by obtaining I-V characteristic curves and their response to illumination prior to and after the impedance measurements.

Figure 4.5. Photograph of evaporation system used to deposit Al contacts on the film surface.
4.3. Current-Voltage Characteristic Curve Measurements for a-Si:H Solar Cells

The experimental apparatus in figure 4.6 was used to produce I-V characteristic curves for a-Si:H solar cells in this project.

Figure 4.6. A photograph of the equipment used for I-V measurements.

In attempting to produce accurate and reliable measurements, the samples have been placed between a sample holder and a mask to prevent them from moving. Measurements have been taken across several equivalent contact spots to examine
different points on the sample, and also for verification of uniformity. The current-voltage characteristic curves were produced in dark and under simulated AM 1.5 global illumination. All measurements have been conducted on p-i-n a-Si:H solar cells at room temperature, in absence of light, when illuminated by white light provided by a high power quartz halogen lamp, and illuminated at different wavelengths (650nm and 950nm) provided by LEDs. A Keithley picoammeter, which provides 10\(^{-11}\) sensitivity range and allowing digital read out, was used to measure the DC output current. A Kepco bipolar power supply was employed to apply a variable voltage. An X-Y chart recorder was used to draw the I-V curves.

The I-V curves produced under various illumination intensities were in good agreement with the results found by impedance spectroscopy (IS) technique. The red and IR radiations have shifted the curve downward slightly from its equilibrium condition indicating an increase in the current density. From the curves, open circuit voltage (\(V_{oc}\)), short circuit current (\(I_{sc}\)), fill factor (\(FF\)), and the efficiency as well as shunt and series resistances may be determined. These parameters with diode quality factor (\(n\)) and dark saturation current (\(I_d\)) are crucial to obtain information about carrier transport mechanism. Hence, the photovoltaic properties of the cell may be evaluated.

Deterioration in performance of photovoltaic solar cells, particularly a-Si:H, during prolonged illumination was first observed by Staebler and Wronski [1977]. To investigate this phenomenon in this project, the sample was light soaked for up to 60 hours. The cell temperature was controlled by mounting the cell on a copper block
with water cooling to prevent any annealing effect. The I-V characteristic curves have been measured after 2, 20, and 60 hours of light soaking for dark and illumination. A slight improvement in efficiency was observed after 2 hours of light soaking, the cell then started to degrade.


4.4.1. Light Soaking of The Sample.

It is well known that the performances of amorphous silicon solar cells are degraded significantly when they are exposed to prolonged illumination [Staebler and Wronski, 1977], as mentioned in previous chapters. The degradation is associated with creation of metastable recombination centres that reduce the diffusion length and metastable traps that can distort the internal field distribution [Carlson, 1987].

In this work, we have investigated the efficiency degradation of p-i-n a-Si:H solar cells by light soaking the sample for up to 60 hours at room temperature in the lab. The sample was exposed to simulated global AM 1.5 radiation for 60 hours. The cell’s temperature was controlled by blowing air on it, to avoid any self annealing effect. The I-V characteristic curves were drawn after 2 hours, 20 hours, and 60 hours. The I-V curve after 2 hours supported the evidence indicated by earlier results [Subaer, 1995, Carlson et al., 1997] that the efficiency of p-i-n a-Si:H solar cells improves slightly after short exposure to light and then starts to decline.
Following the light soaking the samples were taken for impedance spectroscopy measurements. The results of comprehensive light soaking degradation process on two different samples are presented in chapter five.

4.4.2. Annealing The Sample

The light-induced degradation in a-Si:H cells can be reversed by annealing at elevated temperatures. This has been shown by various workers over the last three decades [Staebler and Wronski, 1977, Bolko Von Roedern, 1991, Dai Guo-Cai et al., 1989, Carlson et al., 1987, Mahan et al., 1979, Carlson et al., 1997]. Annealing the cell at temperatures above 150 °C was found to restore the initial values [Staebler and Wronski, 1977]. In this part of the project, we describe the experimental procedure that was used to probe the recovery of our degraded p-i-n a-Si:H solar cell.

Following the light soaking, the sample was put on a metallic sample holder and placed into a vacuum chamber to avoid any external effects. Hydrogen gas was flowed through the chamber to prevent any oxidation. A tungsten heater was used to increase the temperature inside the chamber. The sample temperature was kept at 150 °C for one hour and left to cool down naturally in the chamber. Finally, the sample was brought back for I-V characteristics proceeding and then IS measurements.
4.5. Experimental Procedure of Impedance Spectroscopy (IS)

Dark and illuminated IV characteristics were recorded, on the samples described in section 4.2.2, before and after the impedance spectroscopy measurements commenced.

The impedance spectroscopy measurements were performed using the experimental arrangement shown in figure 4.8. The sample was affixed on a sample holder to prevent movements in order to avoid damaging the contacts and then placed in a vacuum chamber to eliminate external affects on the impedance measurements. The chamber was connected to a pipe to enable cooling of the sample using liquid Nitrogen (N). This chamber was put inside a big black box to block external light while making the dark measurements. The white light was provided by a quartz-halogen globe to simulate AM1.5 solar spectrum. Sub-bandgap illumination was provided by LED's with centre wavelengths at 650 and 950 nm. The output signal from the cell was fed into a very high precision AC bridge analyser (WAYNE KERR 6425). This AC bridge analyser, widely used for impedance spectroscopy in electrochemistry, was interfaced to a personal computer via an RS232-C line for automatic data collection. The program Procomm was used to receive the data from the AC bridge. Since, the values of the variables which appeared on the analyser’s screen were accompanied by units, writing a program to separate the numerical data from the units was needed. So, a filenom program in lahey personal 77 Fortran was written for this purpose. The cleaned data was saved on a floppy disk and Excel
Spread sheet was used to determine the values of real and imaginary parts of impedance. The Easy-plot program was employed to produce the impedance plots.

Using the built-in bias voltage provided by the 6425B, measurements were made at different bias voltages, which is equivalent to making measurements at different points on IV characteristic of the cell. All measurements used the 6425B's in-built AC modulation at an amplitude of 100mV. The illumination intensity was constant for each series of measurements.

Light soaking measurements were carried out on sample No.73 (p-i-n junction a-Si:H solar cell). The sample was light soaked for up to 60 hours. Measurements were repeated after 2, 20, and 60 hours to investigate the photodegradation (Staebler Wronski effect) of the cell.
Figure 4.7. Schematic diagram of the equipment used for the impedance spectroscopy (IS) measurements on a-Si:H solar cells.

Figure 4.8. Photograph of impedance spectroscopy equipment used on a-Si:H photovoltaic cells.
CHAPTER 5

RESULTS AND DISCUSSION

Impedance Spectroscopy (IS)

Impedance spectroscopy (IS) has been used to study the performance and degradation of p-i-n a-Si:H solar cells, fabricated by the rf-glow discharge technique. Results presented for dark and illuminated cells, using two different forms of presentation confirm the validity of the technique.

The sub-bandgap energy transitions were investigated by using different energy photons using red and IR lights. The results were compared to those obtained from the I-V curves and two alternative possibilities were suggested.

The photodegradation of the samples was examined by exposure to 60 hours of light soaking. The degradation was assessed in terms of reduction in FF and current density. These reductions in performance were deduced to be due to the production of dangling bonds in the i-layer as a result of the light soaking. The performance of the cell was restored by annealing at 180°C in a vacuum chamber for one hour followed by cooling the sample naturally at room temperature.

5.1 Current-Voltage Characteristic Measurements

The measured characteristic curves of the p-i-n a-Si:H solar cell that were used in this work under AM1.5 global illumination and dark conditions, before starting the Impedance Spectroscopy (IS) are shown in figure 5.1.
Illumination has shifted the curve downward and the cell’s characteristic is
dominated by the series resistance \( (r) \) for voltages greater than the open circuit
voltage, and by the shunt resistance \( (R_{sh}) \) for voltages less than zero. Both series and
shunt resistances are easily obtained from the figure. We have made impedance
spectroscopy measurements on different points on this curve by making
measurements at different bias voltage.
5.2. Impedance Spectroscopy Measurements

5.2.1 Dark Condition

A typical set of results for a p-i-n a-Si:H solar cell in the dark at various reverse bias voltages is shown figure 5.2 and 5.3. The characteristic semicircular curves shown result when the imaginary part of the impedance is plotted against the real part in the complex plane.

![Graph showing impedance spectroscopy results](image)

Figure 5.2. Real \((Z' = |Z| \cos \Psi)\) and imaginary \((Z'' = |Z| \sin \Psi)\), parts of the complex impedance \((Z = Z' - jZ'')\), for an a-Si:H solar cell in dark, plotted in the complex plane. The open circles correspond to zero bias and the open squares, to reverse bias-voltage of 0.2.

The first figure, 5.2, represents the cell in the dark under 0v and 02v reverse bias voltage respectively. These curves appear to deviate dramatically from the semicircular shape. It is unclear at this stage whether these curves would ultimately
become semicircular in form with larger radii, or continue as straight lines. We interpret these deviations from the ideal form by assuming that one or more of the elements of the equivalent circuit are non-linear and their values are a function of frequency. Further measurements would need to be made, to confirm this, at lower frequencies than we have done (the lowest frequency limit of our equipment is 20Hz. This deviation produced a sharp angle with \( Z_{\text{imaginary}} \) axis that was discussed by Suresh [1996] as being due to change in bias voltage. MacDonald [1987], Buck [1987], Pinkowski et. al., [1990], Kohei Uosaki et. al., [1990] and Stieble et. al., [1990], also argued this deviation is a result of the change of the potential in the solution in the case of an electrochemical cell.

![Figure 5.3](image_url)

**Figure 5.3.** Real \((Z' = |Z| \cos \Psi)\) and imaginary \((Z'' = |Z| \sin \Psi)\) parts of the complex impedance \((Z = Z' - jZ'')\), for an a-Si:H solar cell in dark, plotted in the complex plane. The open circles correspond to 0.4 reverse bias and open squares, open triangles, and crosses to bias-voltages of 0.6, 0.8, and 1.0 V respectively.
Figure 5.3 is the characteristic of curves in the dark under higher applied reverse bias voltage. This figure consists of four approximately semicircular curves at 0.4v, 0.6v, 0.8v, 1.0v respectively.

As the applied reverse bias increases from 0.2v the impedance spectrum gets close to being semicircular but tending to an ellipsoidal shape, with various diameters. Following the procedure of Sluyters et. al., [1970] who modelled the electrochemical cell as an equivalent circuit and distinguished between the processes that proceed at different time scales in the cell, we have modelled hydrogenated amorphous silicon solar cell as an equivalent circuit consisting of a dynamic resistance (shunt) and a capacitance (diffusion in dark cell and transition in illuminated cell) in parallel with a resistance in series as shown in figure 5.4.

![Figure 5.4: AC equivalent circuit for a-Si:H solar cell in dark.](image)
As mentioned in previous chapters, the diameter of the curve for each bias voltage corresponds to the dynamic resistance \( R_d \) of the space charge carriers in the depletion region at that particular voltage [Sluyters et. al., 1970], as \( R_p \) is very high and can be neglected. The series resistance \( r \) represents the distance between the origin and the intersection of the curve with X-axis at maximum frequency. From both the figure 5.2 and the figure 5.3 it can be seen that the predominant effect of increasing the applied reverse bias voltage, which is equivalent of making measurements on different points on the I-V characteristic curve, is not only to change shape of the curve but also to decrease the dynamic resistance and overall impedance of the equivalent circuit of the cell. The higher the bias voltage is the smaller the dynamic resistance and the impedance are, whereas the series resistance \( r \) has not been affected by the external applied bias voltage.

These reductions in the values of dynamic resistance \( R_d \) and overall impedance of the cell are shown in 5.3. The highest reverse bias led to the smallest values of impedance and dynamic resistance \( R_d \) of the circuit as might be expected from the form of the IV characteristic. We assumed that all carriers were collected for reverse bias voltage greater than 0.2v and thus, we can exclude the recombination in the depletion region. This can be adequately interpreted as being due to trapping of holes in the valence band tail states and emission back to the band again. The trapping and emission from states at the hole and electron quasi-Fermi level is indicated by the inverse of the frequency at minimum and maximum imaginary part of impedance.
respectively in figure 5.3. However, the effect of applied reverse bias voltage is far better recognised as a pronounced change of the respective impedance spectra by comparing 0v and 1v curves.

In the dark condition the diffusion capacitance \( C_d \) is the dominant parameter beside the dynamic resistance \( R_d \), because the charge carriers cross the p/i and i/n interfaces mostly by diffusion processes rather than drift transition. Hence, the transition capacitance is neglected. The values of \( C_d \) determined experimentally show a gradual increase with increasing the reverse bias voltage. The characteristic time may be determined from the number of trapping events in the defect states and minority carrier lifetime (\( \tau \)) of a localised carrier before re-emission. The minority carrier lifetime (\( \tau \)) was calculated using the following equation:

\[
\tau = C_d R_d / 2
\]

\[
C_d = \frac{1}{\omega Z''}
\]

\[
\omega = 2\pi f \quad f \text{ is the frequency of the measurement}
\]

\( R_d \) was determined experimentally from:
\[ R_d = \left[ \frac{1}{(Z' - r)}(Z' - r)^2 \pm (Z'')^2 \right] \quad [\text{Sluyters- Rehback and Sluyters, 1970}]. \]

These equations are true when the imaginary part of impedance \( (Z'') \) is at its maximum.

The values of diffusion capacitance, dynamic resistance, series resistance and minority carrier lifetime are tabulated in table 5.1. Since the curves at 0v and 0.2v are not semicircular, the accuracy with which the parameters can be determined reduces therefore, these have not been tabulated for these particular voltages.

<table>
<thead>
<tr>
<th>Bias(V)</th>
<th>( C_d )(nF)</th>
<th>( R_d )(kΩ)</th>
<th>( \tau )(Ω)</th>
<th>( \tau )(μsec) = ( R_d C_d / 2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>0.2</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>0.4</td>
<td>1.87</td>
<td>220</td>
<td>100</td>
<td>205.7</td>
</tr>
<tr>
<td>0.6</td>
<td>4.08</td>
<td>156</td>
<td>100</td>
<td>318.2</td>
</tr>
<tr>
<td>0.8</td>
<td>5.8</td>
<td>104</td>
<td>70</td>
<td>301.6</td>
</tr>
<tr>
<td>1.0</td>
<td>7.07</td>
<td>80</td>
<td>50</td>
<td>282.8</td>
</tr>
</tbody>
</table>

Table 5.1. Calculated solar cell parameters for dark sample.
5.2.2 Illumination Condition

Figure 5.5 shows the impedance of an a-Si:H photovoltaic cell under absorbed global AM 1.5 radiation at room temperature. The change in the parameters at various values of the applied reverse bias voltage was demonstrated in a similar manner to figure 5.3.

![Graph showing impedance](image)

**Figure 5.5.** The real ($Z' = |Z|\cos\Psi$) and imaginary ($Z'' = |Z|\sin\Psi$) parts of the complex impedance ($Z = Z' - jZ''$), for an a-Si:H photovoltaic cell exposed to simulated AM 1.5 illumination.

Theoretical impedance curves based on the values of $R_s$ and $C_T$ measured from the plots in figure 5.5 are shown in figure 5.6. The bias voltages were as for figure 5.5 and series resistance set to zero for simplicity, as it is small compared to $R_s$. 
Figure 5.6 The theoretical impedance of the circuit plotted in the complex plane. The Value of $R_d$ and $C$ were obtained from the results of figure 5.5. ($Z' = |Z| \cos \Psi$) and ($Z'' = |Z| \sin \Psi$). The bias voltages were as for figure 5.5.

In comparing the experimental curves with their theoretical counterparts; the experimental curves of figures 5.3 and 5.5 are slightly distorted, being somewhat flattened in the X direction and Y direction respectively compared to full semicircles. Illumination creates photogenerated electrons and holes in the i-layer which drift to the contacts under the influence of internal electric field. As a result a great reduction in the bulk recombination occurred. These reductions lead to considerable decrease in the impedance of the equivalent circuit and dynamic resistance ($R_d$).
In figure 5.5, illumination has decreased the dynamic resistance \( R_d \) and the overall impedance of the equivalent circuit of the device dramatically. The illuminated impedance is less than its dark counterpart by more than 150 times at 0.4v reverse bias voltage, and the dynamic resistance \( R_d \) has decreased by more than 200 times at the same bias. Similar reductions occurred at different bias voltages. The illumination has improved the photoconductivity of the cell significantly, attributed totally to band to band transitions that occur when all traps within the mobility gap are saturated. The AM 1.5 global illumination, at room temperature was sufficient to ensure that this was the case.

The decrease in \( Z \) and \( R_d \) is more pronounced with increasing reverse bias voltage. Increasing the applied reverse bias voltage has increased the internal electric field which depletes the i-layer to a greater extent and prevents further recombinations in the bulk states. As a result, the dynamic resistance \( R_d \) and the impedance of the equivalent circuit decreased further with increasing the bias. These decreases are accompanied by increases in the values of the transition capacitance. As we increased the reverse bias from 0v to 1v the transition capacitance increased from 23nF to 100nF. This indicates that the bias has increased the photogenerated carriers by more than four times.

Remarkable changes in series resistance \( r \) have not been observed with either illumination or variation of applied reverse bias voltage, while the transition capacitance has been increased significantly with both parameters compared to their dark counterparts as shown in table 5.2. The transition capacitance has been used, in
this case, because the drift mobility is much higher than that for the diffusion mobility. As a result, the transition capacitance dominates the total capacitance and is no longer negligible. The equivalent circuit for this is shown in figure 5.7.

![Figure 5.7 AC equivalent circuit for a-Si:H solar cell under AM 1.5 global illumination.](image)

The values of dynamic resistance, series resistance, transition capacitance, and minority carrier lifetimes (τ) may be obtained from the plots as previously shown for figure 5.3 [Sluyters-Rehback and Sluyters, 1970]. The values of the minority carrier lifetimes (τ), that been calculated in this study, are within the same range as those obtained for similar material by Open Circuit Voltage Decay (OCVD) technique [Madan et al., 1979; Green, 1983; Cornish et al., 1995] and are between (100μs-400μs) for dark cell and under 50μs for illuminated cell. Thus, in later case, the carriers would travel shorter distances before they are trapped. The transition capacitance at each bias voltage in figure 5.5 is much larger than the diffusion capacitance at the given bias, as may be seen in comparing table 5.1 and table 5.2.
The value of $C_T$ at 0.4v reverse bias voltage is 20 times larger than $C_d$ at the same bias. This difference in the capacitance was caused by AM 1.5 global illumination. A photon of energy ($h\nu$), which is high enough to overcome the work function energy, excites an electron from the valence band to the conduction band. This mechanism leaves a hole in the valence band creating an internal electric field across the cell which increases with increasing reverse bias voltage as mentioned previously.

<table>
<thead>
<tr>
<th>Bias(V)</th>
<th>$C_T$(nF)</th>
<th>$R_d$(kΩ)</th>
<th>$r$(Ω)</th>
<th>$\tau$(μsec) = $R_d C_T/2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>23</td>
<td>2.9</td>
<td>56</td>
<td>33.35</td>
</tr>
<tr>
<td>0.2</td>
<td>33</td>
<td>1.37</td>
<td>39</td>
<td>22.6</td>
</tr>
<tr>
<td>0.4</td>
<td>38.5</td>
<td>0.93</td>
<td>39</td>
<td>17.9</td>
</tr>
<tr>
<td>0.6</td>
<td>54</td>
<td>0.82</td>
<td>31</td>
<td>22.1</td>
</tr>
<tr>
<td>0.8</td>
<td>96</td>
<td>0.69</td>
<td>22</td>
<td>33.1</td>
</tr>
<tr>
<td>1.0</td>
<td>100</td>
<td>0.6</td>
<td>22</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 5.2. Calculated solar cell parameters for illuminated sample.

The impedance spectroscopy technique allows the results to be presented in different ways as mentioned previously. Figures 5.8, 5.9, 5.10 and 5.11 show an alternative
manner of presenting the same measurements which highlight the change of impedance with frequency. In this case we have plotted the real and imaginary components of the impedance from figures 5.6, 5.2, 5.3 and 5.5 respectively, as a function of logarithmic frequency. This presentation manner of the data can be very beneficial in suggesting the presence of various physical processes leading to the overall response.

![Graph](image.png)

**Figure 5.8.** Theoretical imaginary and real parts of the impedance as a function of frequency for the same sample.

At frequencies less than 1kHz ($f<1000$) the theoretical curves show a horizontal constant line. The curves change rapidly between $1kHz<f<50kHz$ followed by stabilised constant line at very high frequencies. Figures 5.9-5.11 show the forms of the experimental curves plotted in the same manner as figure 5.8.
Figure 5.9. The real and imaginary parts of the impedance as a function of frequency for dark case.

Figure 5.10. The real and imaginary part of impedance as a function of frequency for dark case.
The experimental curves of figure 5.9 (dark under 0v and 0.2v) are interesting in that they conform closely with the expected form at a sufficiently high frequency, but do not turn over and become nearly constant at the lowest frequencies measured. It is probably likely that they would do this if measurements were extended to sufficiently low frequencies.

The curves in dark at 0.4v-1.0v bias voltages are complying with their theoretical counterparts in figure 5.8, except a slight deviation at 0.4v reverse bias voltage has occurred as shown in the figure 5.10.

In both figures 5.9 and 5.10 the change in the form of the curves is less rapid than in the theoretical curves indicating frequency dependent processes in this region.

Figure 5.11. The real and imaginary parts of the impedance as a function of frequency for illumination case.
The form of the experimental curves seen in figure 5.11 shows the Bode plots for illuminated cell at the same bias voltages of figure 5.5. In comparing this figure to the theoretical counterpart (figure 5.8) a slight deviation from the constant values of impedance at low frequencies \( f<1\text{kHz} \) has occurred followed by a rather flatter slope than the abrupt slope which was observed in figure 5.8 at higher frequencies \( 1\text{kHz}<f<50\text{kHz} \). Then returning to the steady state at lower values of impedance.

We interpret these as due to processes involving the minority carrier lifetime and trapping/detrapping of these carriers. The minority carrier lifetime would affect the response in the high frequency region, and trapping/detrapping would affect the response in the low frequency region.

### 5.3. Impedance-Voltage Measurements

As described in previous sections, the effect of illumination on the impedance is dramatic. This effect is even more clearly seen in figure 5.12 in which the impedance is plotted as a function of bias voltage, for the same cell under illuminated and dark conditions, at room temperature and constant frequency (10kHz). This figure shows that the photogenerated voltage has shifted the complete curve to higher bias voltages. The maximum impedance occurs at the bias voltage corresponding to the photovoltage which is in good agreement with the value shown by the I-V characteristics in figure 5.1. The impedance under illumination is considerably smaller, by a factor of \(~25\), than the dark impedance.
Figure 5.12. Impedance plotted as a function of bias voltage for a-Si:H solar cell, at room temperature and for a modulation frequency of 10kHz. The values for curve under illumination have been multiplied by 25 before plotting.

5.4. Sub-Bandgap Transitions in a-Si:H Solar Cells

The I-V characteristics of p-i-n a-Si:H solar cell under infrared (IR) and red illumination at room temperature are shown in figure 5.13. These illuminations have shifted the curve downward on the current axis slightly as expected. The current density in these cases is, as expected smaller than that obtained under AM1.5 illumination. The open circuit voltage is also changed from its value under high intensity white light.
In order to investigate the production of photogenerated carriers in p-i-n a-Si:H solar cells by using sub-bandgap energy photons, the cell was illuminated by red ($\lambda=650$nm) and IR ($\lambda=950$nm) lights. The impedance spectroscopy measurement results were presented in the same manner as in figures 5.3 and 5.5.
Figure 5.14. The imaginary part of impedance plotted against the real part for dark, infra red, and red lights at 0v bias voltage and room temperature.

Figure 5.14 shows the experimental curves of the cell under red, IR, and AM 1.5 illuminations as well as in the dark at 0v bias voltage and at room temperature. The dark and AM1.5 illuminated curves that have previously have discussed were put in the figure to show the differences. The red and IR curves show good semicircular shapes, except for a slight deviation from the ideal semicircle in both cases. These deviations are attributed to the trapping /detrapping and minority carrier lifetimes in the i-layer, as previously discussed. The impedance of the equivalent circuit and the dynamic resistance (the diameter of the semicircle) in these cases are significantly larger than AM1.5 and smaller than the dark counterparts. The values of $Z$ and $R_d$ are further decreased with increasing applied reverse bias voltage as shown in figure 5.15.
Figure 5.15. The imaginary part of impedance plotted against the real part for dark, infra red, and red lights at 1V bias voltage and room temperature.

The values of $R_d$ in both curves have been reduced to less than a half and $Z$ has reduced by 1.5 times as the reverse bias increased to 1V. It was not expected that the curves produced under sub-bandgap radiation would be significantly different from the dark curves. However, the curves for both the red and IR indicate an increase in conductivity compared to the dark case. We believe this increase occurred as a result of two possible mechanisms. Firstly, the photoconductivity may be attributed to two-step excitations. The second possible process is that, the band tails of both valence and conduction bands extend into the mobility gap. A single photon energy (hv) might be sufficient to excite the electron from the extended valence band tails to
the extended conduction band tails. Thereby, electron/hole pair may be generated in
the external circuit and hence improve the photoconductivity. These observations
agreed with the results obtained from the I-V characteristic curves in figure 5.13.

![Impedance graph](image)

Figure 5.16. Impedance plotted as a function of bias voltage for a-Si:H solar cell at room temperature
and fixed modulated frequency of 10kHz. The measurements are for dark, IR, red, and white light.

Figure 5.16 describes the variation in impedance of the equivalent circuit as a
function of the applied reverse bias voltage for dark, white, red, and infrared
illuminations. The dark curve (open circles) increases with increasing the bias
voltage and reaches its maximum value at 0v bias voltage. The impedance peak
gradually decreases as the bias voltage passes the 0v in positive direction. Finally,
the impedance has stabilised at 1.7v bias voltage. The next curve below this
(diamonds) is the cell under IR illumination. The peak of the impedance has occurred at 0.4v. The photogenerated voltage has shifted the complete curve to higher bias voltage as previously observed for white light as shown in figure 5.12.

The same behaviour of the impedance has been observed with increasing the bias voltage. Similar behaviour under the red and the AM1.5 illumination were observed, except that the impedance maximum occurred at 0.6v and 1v respectively. The value of dark impedance is considerably higher and AM1.5 illumination impedance lower than the sub-band illumination impedances. These photogenerated voltages are proportional to the photon energies supplied by each particular illumination. The shifting of the curves was assigned being due to as the variations in the photovoltage created by different photon energies, and the stretching of the curves was attributed to a bulk property effect of the cell. It is apparent from the figure that the sub-bandgap photon energies that are provided by red and IR light are much less than those of white light photons. This means that band to band transition by sub-bandgap photons is impossible. Hence, multiple sub-bandgap photons are needed to create an electron/hole or a single photon needed in case of extended band tails into the optical gap as a result of high light intensity. These results agreed with those found by Daxing Han and co-worker Wenhao Wu [1987] and Cohen et al., [1982].
5.5. Capacitance-Voltage measurements

Capacitance-Voltage measurements were employed to investigate the dependence of the photocapacitance and the effect of the illumination on p-i-n a:Si:H solar cell performance. The measurements were carried out under AM1.5 radiation at room temperature and fixed frequency of (10kHz). We have defined the photocapacitance ($C_{ph}$) as the value of the equilibrium (the cell in the dark) capacitance ($C_{dk}$) subtracted from its value under the illumination ($C_{im}$). This photocapacitance was used as a barometer to examine the i-layer electric field and photogenerated carriers with illumination and applied bias voltage which would assess the performance of the cell.

The results are given in figure 5.17-5.19. In figure 5.17, the plot basically indicates a linear relationship between the photocapacitance and the applied bias voltage for low values of bias voltage. The most logical explanation of this is that the reverse bias voltage adds to the stress of the original electric field in the i-layer and causes further displacement of the mobile space charge carriers. Figure 5.18 shows the reciprocal of the square root of the photocapacitance as a function of bias voltage. The intercept of the straight line with the X-axis corresponds to the built-in voltage of the cell which is about 0.3v in our cell. We plotted the reciprocal square of the photocapacitance as a function of bias voltage in the same figure (5.18) which also shows a linear relationship with bias voltage. The effect of illumination and bias voltage on the number and distribution of current carriers is illustrated in figure 5.19. Initially, (a) (dark cell), a small number of the charged carriers are trapped in the localised states in such a way that each electron is associated with a hole throughout the i-layer.
In step (b) (illuminated cell), there are many more carriers which tend to be swept away towards the interfaces under the induced i-layer electric field. Illumination has detrapped some of the trapped electrons by providing them separation energy these drift to the contacts under the effect of the induced field. Finally, step (c) at low bias voltage (no.1) some of the charge carriers still remained trapped in the deep states and the rest have drifted to the n/i and i/p contacts. The electric field increased significantly as the bias voltage was increased (2&3) holes and electrons are pushed apart towards the interconnections as a result. Thereby, one can conclude from the above steps that the photocapacitance \( C_{ph} \) depends on both illumination and the applied bias voltage.

<table>
<thead>
<tr>
<th>Bias Voltage(V)</th>
<th>( C_{ill} ) (nF)</th>
<th>( C_{dk} ) (nF)</th>
<th>( C_{ph} = C_{ill} - C_{dk} ) (nF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1</td>
<td>1.263</td>
<td>1.257</td>
<td>0.006</td>
</tr>
<tr>
<td>-0.9</td>
<td>1.264</td>
<td>1.257</td>
<td>0.007</td>
</tr>
<tr>
<td>-0.8</td>
<td>1.2645</td>
<td>1.2575</td>
<td>0.007</td>
</tr>
<tr>
<td>-0.7</td>
<td>1.266</td>
<td>1.22575</td>
<td>0.0085</td>
</tr>
<tr>
<td>-0.6</td>
<td>1.266</td>
<td>1.2587</td>
<td>0.0073</td>
</tr>
<tr>
<td>-0.5</td>
<td>1.269</td>
<td>1.259</td>
<td>0.01</td>
</tr>
<tr>
<td>-0.4</td>
<td>1.278</td>
<td>1.262</td>
<td>0.016</td>
</tr>
<tr>
<td>-0.3</td>
<td>1.305</td>
<td>1.266</td>
<td>0.039</td>
</tr>
<tr>
<td>-0.2</td>
<td>1.333</td>
<td>1.269</td>
<td>0.064</td>
</tr>
<tr>
<td>-0.1</td>
<td>1.365</td>
<td>1.272</td>
<td>0.093</td>
</tr>
<tr>
<td>0</td>
<td>1.4</td>
<td>1.275</td>
<td>0.125</td>
</tr>
</tbody>
</table>

**Table 5.3.** Corresponding values of photocapacitance at different bias voltages calculated experimentally.
Figure 5.17. Photocapacitance plotted as a function of bias voltage for a p-i-n a-Si:H solar cell.

Figure 5.18. Reciprocal square and reciprocal of the square root of the photocapacitance vs Bias voltage for p-i-n a-Si:H solar cell.
a) Dark cell.

b) Illuminated cell.

c) Under effect of bias voltage.

**Figure 5.19.** Step by step illustration of effect of illumination and bias voltage on photocapacitance in a-Si:H solar cells.
5.6. Light-induced degradation in a-Si:H solar cell

The highest efficiency in hydrogenated amorphous silicon manufacturing is 9.5% reported by Sanyo in 14th European Photovoltaic Solar Energy Conference and Exhibition, and multi-junction cells and modules were produced with 11.1% stable [Guha 1997]. Nonetheless, the Staebler and Wronski effect is still facing amorphous silicon solar cell technology and has remained unsolved for the time being.

The electronic properties of hydrogenated amorphous silicon solar cells are degraded when they are exposed to prolonged band-gap light [Staebler and Wronski 1977]. Long exposure to light decreases both photoconductivity and dark conductivity of this material. Subsequent work [Staebler et al. 1977], showed that the performance of the a-Si:H solar cells was also reduced by light soaking, and that the degradation could be reversed by annealing at elevated temperature. Annealing at a temperature above 150 °C was found to restore the initial values. The rate of degradation and reversal process depends on the external conditions (temperature, intensity, and applied bias voltage). A high annealing temperature, strong light intensity, and large applied reverse bias voltage will accelerate the recovery [Carlson et al., 1996].

The recovery process is thermally activated and involves local hopping of the hole over a barrier. Hence, annealing temperatures between 150-180°C thermally generate electrons and holes which then drift to opposite side under the built-in electric fields and restore the initial performance. It is noteworthy to mention that
temperatures higher than 180°C in fact worsen the cell’s performance or damage the cell completely.

Since the degradation and annealing involve electrons and holes hence, the electric field has a large effect on both processes. The initial built-in electric field is generally enhanced by applied reverse bias voltage, as previously discussed in this chapter. A strong field decreases the probability of both trapped electrons and holes residing in the same defect complex so that the rate of creation of new metastable centres is quite low as compared to the open-circuit situation.

In this study, the experimental results of impedance spectroscopy response before and following photo-induced reversible changes for the same sample of a-Si:H p-i-n solar cells are presented. Based on detailed analysis of these results, a complementary explanation of light-induced changes in p-i-n solar cell is suggested.

Light soaking experiments using AM 1.5 illumination were carried out on two samples of p-i-n a-Si:H solar cells prepared under the same conditions. The initial and light soaking parameters of the cells are tabulated in tables 5.4 and 5.5. The samples were light soaked for up to 60 hours while maintaining the cell’s temperature close to room temperature by blowing air on it throughout the light soaking, to avoid any possible self annealing.
Table 5.4. Calculated cell parameters of single junction a-Si:H solar cell. Sample No. 73. The cell deposited under normal condition.

<table>
<thead>
<tr>
<th>Time</th>
<th>$J_{sc}$(mA)</th>
<th>$V_{oc}$(v)</th>
<th>FF</th>
<th>$\eta%$</th>
<th>$R_{sh}$(kΩ)</th>
<th>$R_s$(kΩ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>14.28</td>
<td>0.75</td>
<td>0.5</td>
<td>5</td>
<td>9.500</td>
<td>0.25</td>
</tr>
<tr>
<td>2 hours</td>
<td>14.65</td>
<td>0.75</td>
<td>0.55</td>
<td>5.65</td>
<td>8.250</td>
<td>0.3</td>
</tr>
<tr>
<td>20 hours</td>
<td>4.49</td>
<td>0.77</td>
<td>0.326</td>
<td>1.128</td>
<td>6.0</td>
<td>0.7</td>
</tr>
<tr>
<td>60 hours</td>
<td>3.2</td>
<td>0.81</td>
<td>0.295</td>
<td>0.765</td>
<td>3.750</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 5.5. Calculated cell parameters of single junction a-Si:H solar cell. Sample No. 250. The cell deposited under normal condition.

The shunt and series resistances were calculated from the slope of the I-V curves at 0v and open circuit voltage condition respectively. From the tables above one may see a gradual increase in the series resistance ($R_s$) with light soaking, accompanied by a significant decrease in the shunt resistance ($R_{sh}$) for the cell. This increase in
\( (R_s) \) would withstand the primary photocurrent and decreases the photoconductivity of the cell. The shunt resistance was decreased to 39\% of its as deposited value, whereas the series resistance was increased by eight fold after 60 hours of light soaking.

In figure 5.20 we show typical current-voltage curves for the as-deposited cell and after 60 hours of light soaking at room temperature to display the effect. The cell’s characteristics in each case are dominated by the series resistance for voltages greater than the open circuit voltage, and by shunt resistance for voltages less than zero.

![Graph showing current-voltage curves](image)

**Figure 5.20.** I-V Characteristic curves for a-Si:H solar cell used in this work.

The large decrease in shunt resistance and increase in series resistance, after 60 hours of light soaking, have contributed to the reduction in the fill factor, current density,
and subsequently the efficiency of the cell. Degradation was evaluated in terms of fill-factor (FF) and current density (Jsc) changes. Figure 5.21 shows for the fill-factor changes for both samples as a function of time of light soaking.

![Figure 5.21. Fill factor changes after 60 hours of light soaking. Circles indicate sample No. 73 and squares sample No. 250.](image)

As it can be seen from the figure, a slight improvement occurred after approximately the first two hours of light soaking. This was followed by a relatively rapid decline which then slowed down significantly and reached the final stabilised condition after 60 hours. The time dependence of the degradation shown by the fill factor curves can be fitted to a stretched exponential. Within 2 hours of the light soaking, the initial value of fill factor of sample no.73 (table 1) had increased to 0.55 followed by a
drop and stabilised at 0.295. We interpret the slight improvement after 2 hours of the light soaking as due to the fast changes in the internal fields in the i-layer, which is determined by external conditions (intensity and temperature) Bolko Von Roedern [1991], Baban et al., [1997].

![Figure 5.22. Current density variations with light soaking. Circles represent sample No. 73 and squares sample No. 250.](image)

In the present results, the fill factor dropped down to approximately 73% of the initial value. However, the degradation of the solar cell is not only related to the reduction in the fill factor, but also to the reduction in the short circuit current, which makes a major contribution to the degradation process shown in figure 5.22. The fill factor and current density reduction following the light soaking, may be related to
the decrease in the internal potential of the i-layer. The electric field in this region plays the important role of collecting the photogenerated electrons and holes and transporting them to the electrodes where they can be usefully collected. The reduction of electric field is in turn related to the generation of metastable defects, which are dangling bonds formed due to Si-Si and Si-H, in the i-layer of the solar cell.

Figure 5.23. Open circuit voltages a function of light soaking for both samples.

A significant decrease in short circuit current ($I_{sc}$) that has not been compensated by open circuit voltage ($V_{oc}$), was observed after 60 hours of light soaking, as $V_{oc}$ remains relatively constant as may be seen in figure 5.23. This decrease in $J_{sc}$ lead
to a great reduction in the power output. These changes in short circuit current and fill factor caused a significant decrease in the cell's efficiency.

![Figure 5.24](image.png)

**Figure 5.24.** Efficiency decline as a result of light soaking.

The efficiency of the cell dropped to approximately one third of its initial value after light soaking as shown in figure 5.24. This result is in a good agreement with those found by Zhou et al., [1991], Boiko von Roedern [1991], and Hack and Shur [1985]. The initial slight improvement in the performance was inferred to the conversion of charged dangling bonds into the neutral ones, which occurred as a result of fast changes in the operating conditions as previously mentioned. In addition,
illumination at 100 \text{mWcm}^{-2} creates excess carriers that populate the extended and localised band edge states which saturate the defects in the i-layer and increase the photoconductivity of the cell. A similar improvement after a short period of time was observed by Bolko Von Reodern [1991] who studied the fast changes in performance of a-Si:H solar cells.

The sharp decline in the performance following the initial improvement was attributed as being due to formation of excess defect states out of neutral dangling bonds. These defect states increase the density of states (DOS) significantly which lead to a large increase in carrier recombination in the bulk of the material. A high recombination rate of the photogenerated carriers in the i-layer reduces the minority carrier lifetimes which reduce the photoconductivity and limit the performance of the cell. Since, light soaking increases the density of states in a-Si:H solar cells, the saturation of such material is less likely and band to band transitions are unlikely. As a result of these mechanisms, the photoconductivity is decreased which lead to degradation in the efficiency.

The monotonic decrease in the efficiency after 20 hours reflects the role of the depletion region in limiting the collection of carriers; the decrease of the efficiency with time of light-soaking reflects the effect of the increasing density of light-induced defects in the intrinsic a-Si:H.

The saturation of the degradation process of our samples is described by exponential behaviour in figure 5.24. This degradation came close to a halt after 60 hours of steady state exposure conditions and reached its stabilised state. The degradation mechanism in a-Si:H solar cells may involve trapping of photogenerated carriers in
the vicinity of the weak Si-Si bonds located near to a Si-H bond as assumed by Dersch et al., [1981] and Carlson et al., [1997]. These photogenerated carriers could be trapped and localised on the Si-Si bonds and a hole momentarily is localised on the Si-H bond. Although, it is highly likely that either the electron and the hole hop to each other and recombine, there is the possibility that the localised hole will allow the hydrogen atom to move to the trapped electron as a proton and weak Si-Si bond creating a new Si-H. As a result of this incident, hence, two new separated dangling bonds are created which act as strong recombination centres. The transitions in a-Si:H solar cells normally occur in a threefold coordinated silicon (dangling bonds), $T_3$, distributions. Hence, $2T_3^+ \rightarrow T_3^+ + T_3^-$, conversion of neutral dangling bonds into charged ones is the dominant process.

The changes induced by light are reversed by annealing between 150-180°C. In the present study, annealing at 180°C for 60 minutes returned the performance to its original state following cooling to room temperature. In this process, the charged dangling bonds are converted into neutral ones $T_3^+ + T_3^- \rightarrow 2T_3^+$ which is opposite to the light soaking effect.

During the annealing, the thermally generated electrons and holes drift to opposite sides under the effect of built-in electric field. If, however, the annealing time is sufficiently long, the performance would completely recover. It is notable that, whereas the electrical properties have not been completely recovered in our samples due to some physical processes, the performance did. This will be discussed in the next section.
Recent work by Carlson and Kamala Rajan [1996] showed that the recovery of degraded device is accelerated by applying a large reverse bias voltage during the annealing process, and the speed of the recovery increases with increasing the bias. According to the authors, the high reverse bias voltage removes most of light-induced defects in the dark. The effect of the bias voltage is evidence of the involvement of charged dangling bonds in both the degradation and annealing processes. It is determined that degradation is due to conversion of neutral bonds into two charged dangling bonds, as mentioned earlier, whereas, annealing is the opposite process.

To produce state-of-the-art p-i-n a-Si:H solar cell, the deposition conditions are crucial. Deposition temperature and related optical gap, dark conductivity, and hydrogen content in the i-layer are very important parameters to pay attention to in producing a-Si:H solar cells.

5.7. Impedance spectroscopy measurements after light soaking

Impedance measurements have been used to investigate light-induced degradation in p-i-n a-Si:H solar cells. We analysed our results in terms of overall impedance and dynamic resistance loss of the cell. We have interpreted the loss as a factor associated with a reduction in the i-layer electric field. The decrease in the built-in bias in the depletion region is due to the creation of a large number of metastable defects which cause a dramatic increase in the recombination rate for electrons and holes in this region. We have compared the results before and after 60 hours of light soaking to observe the effect.
Figure 5.25. Real part of impedance plotted as a function of imaginary part for a-Si:H solar cell in dark at 0v bias voltage.

Figure 5.25 shows a characteristic semicircular curve when the imaginary part of impedance is plotted against the real part in the similar manner to those plotted before light soaking, for the dark, as deposited and after 60 hours of light soaking at zero bias voltage at room temperature. The impedance after 60 hours light soaking decreased dramatically and forms a better semicircular curve than that for the as deposited curve. This decrease is more pronounced in figure 2.26 where characteristic semicircular curves were plotted for the same cell at 1v bias. The figure shows as deposited, after 2 and 60 hours of light soaking as well as the
annealing curve. The values of impedance were decreased four fold and the dynamic resistance by more than 5 times after 60 hours, whereas both quantities, the impedance and the dynamic resistance, at 2 hours were slightly larger than that of as deposited ones as expected.

Annealing returned the curve to almost its original position. These results were in agreement with those obtained by I-V curves and consistent with results found by Hank et al., [1985] and Zhou et. al., [1991].

Figure 5.26. Real part of impedance plotted as a function of imaginary part for dark cell at 1v bias voltage.
The temperature rise and light intensity will excite the carriers thermally and a number of photogenerated carriers may be produced at the contacts, which in turn increase the build-in electric field in the depletion region. Illumination supports carrier transitions further by exciting the carriers and gives them enough energy to overcome the Fermi-level and reach into the conduction band. Similar decreases in $Z$ and $R_d$ occurred under illumination for both 0v and 1v conditions. The significant decrease in the impedance and $R_d$ may be attributed to the recombinations in bulk due to creation of excess charged dangling bonds as a result of long light soaking.

Figure 5.27. Imaginary part of impedance as a function of real part, before and after light soaking under AM 1.5 irradiance illumination at 0v bias.
Figure 5.28. Imaginary part of impedance as a function of real part, before and after light soaking under AM 1.5 irradiance illumination at 1V bias.

Sub-bandgap energy illumination had similar effect on the impedance plots as the AM 1.5 global illumination and dark cell. In figure 5.29 and figure 5.30 the real part of impedance is plotted as a function of imaginary part for infrared and red light respectively in the same manner as figures 5.25-5.28. It is obvious from these figures that both the dynamic resistance and overall impedance of the equivalent circuit decreased dramatically after 60 hours of light soaking. Further reduction in dynamic resistance and impedance was observed with the application of a reverse bias voltage.
Figure 5.29. Imaginary part of impedance as a function of real part, before and after light soaking for cell illuminated with IR. a) at 0v bias, b) at 1v bias.
Figure 5.30. Imaginary part of impedance as a function of real part, before and after light soaking for cell illuminated with red light. a) at 0v bias. b) at 1v bias.
In comparing the above figures we have found that sub-bandgap impedance curves are located between dark and AM 1.5 global illumination. This is consistent with their photon energies being less than those for white illumination and not being sufficient to produce band to band transitions as the later dose. Therefore, the two steps excitation of photogenerated carriers by infrared and red energies described earlier are quite possible and practical in the interpretation of carrier transition in a-Si:H solar cells.

To investigate the recovery of the performance, we have annealed one of our samples at 180°C. The cell was put into a vacuum chamber, as described in chapter 3, to avoid external effects such as oxidation in the air. As expected, the performance of the cell completely recovered after annealing. The conversion of charged dangling bonds into neutral ones occurs thermally through excitation of electrons and holes into conduction and valence bands.

For a given material; there is sufficient evidence to prove that the charged dangling bonds are limiting the transport properties for both electrons and holes [Bolko Von Roedern 1991, Dai Guo-Cai et al. 1988, and M. Shur 1985]. Hence, the conversion of dangling bonds in the i-layer should be considered in investigating the dark conductivity and photoconductivity of a solar cell.
CHAPTER 6
CONCLUSIONS AND FURTHER WORK

6.1 Conclusions
This work has traced the use of impedance spectroscopy (IS) technique in the characterisation of p-i-n hydrogenated amorphous silicon photovoltaic films fabricated by RF-glow discharge technique, generally called plasma enhanced chemical vapour decomposition (PECVD). The technique was employed on different samples to confirm the results.

A simple p-i-n a-Si:H solar cell was used in this work, with just over 5% efficiency without using highly reflecting back contacts or texturing. The study also included the calculation and determination of induced photocapacitance that was investigated by using capacitance-voltage measurements. The cell’s parameters (fill factor, current density, and open circuit voltage) were reasonably good. The absorption coefficient and optical energy gap of the samples were measured previously by a fellow researcher (Dr. Kazimierz Luczak).

The current-voltage characteristic curves of the sample in the dark and under illumination before and after the light soaking was drawn for comparison. From the curves the cell’s parameters (fill factor, current density, and efficiency) were determined and the degradation was assessed after 60 hours of light soaking. The cell’s characteristics before and after degradation mechanism are dominated by the series resistance for voltages greater than the open circuit voltage, and by shunt resistance for voltages less than zero.
Initially the impedance spectroscopy technique investigations have shown different processes that proceed at different time scales in electrochemical cell. This work investigated these processes in p-i-n junction a-Si:H solar cells. The microscopic mechanisms within the material; density of states and the generation and the lifetime of both charged carriers were closely related to these processes. The results with simple modifications, allowed us to model the cell as an equivalent circuit and determine its parameters, which in turn may be closely related to the performance and stability of the cell.

The flattening and fullness of the experimental curves in figure 5.3 and figure 5.5 is obvious indication two processes occurred. These processes are the minority carrier lifetime which would affect the frequency response of the cell in high frequency and trapping/detrapping which would affect low frequency response region. Hence, the curves would be stretched or foreshortened by these processes. The impedance curve in figure 5.8 shows this effect more clearly, where the transition from high to low impedance occurs more slowly than in the theoretical curves of figure 5.11.

The light dependence of a p-i-n sample was investigated by illuminating the cell by AM1.5 global irradiance. The significant decrease of the dynamic resistance (Rd) and the overall impedance of the equivalent circuit was attributed to the created excess electron/hole pairs at the contacts. Under the illumination, the electrons are excited from extended valence band edge to extended states above the conduction band, leading to a large increase in the photoconductivity. The transition capacitance has been used in this case because the drift mobility dominates the transition photocurrent in the depletion region.
been used in this case because the drift mobility dominates the transition photocurrent in the depletion region.

The effect of the external field was examined by the application of applied reverse bias voltage. The parameters of the equivalent circuit and the impedance have been dramatically affected with increasing the applied reverse bias voltage. A significant decrease of both dark and illuminated impedances was deduced to be due to the enhancement of the original electric field of the cell, which displaces the photogenerated carriers toward the contacts.

The semicircular impedance curves of a-Si:H films, illustrated in the previous chapter, indicates that the AC equivalent circuit consists of a dynamic resistance ($R_d$) and a capacitance (C) in parallel connected to a series resistance ($r$). The diameter of the semicircle represents the dynamic resistance of the cell, and $r$ describes the distance between the origin and the intersection of the maximum imaginary impedance with X-axis. Since the transition current was dominated by diffusion in the dark and by drift in the illumination, the (C) was denoted by $C_d$ for dark cell and by $C_T$ for illuminated cell respectively. The consideration of the transition capacitance in the equivalent circuit, for the illuminated cell, agreed with the interpretation of Kohei et al. [1990]. An increase in the drift current toward the contacts by optical transitions was attributed to the increase in the photogenerated carriers near or within the conduction band edge.

Based on the experimental results of parameters of the equivalent circuit, we have produced the theoretical curves for each case and for both manners of presentation (Nyquist and Bode) to compare with the experimental results.
The same results were presented in a different manner which is similar to the so-called Bode plot in electrochemistry [Pinkowski et al., 1990]. This alternative manner of displaying the results highlights the variation of the real and imaginary parts of impedance with frequency, provided important information about the two types of processes (fast and slow). These processes enabled additional information to be revealed on minority carrier lifetime changes by using a limited range of frequency. So, below 2kHz the charged carriers will travel longer distances before recombining again in the i-layer, whereas above that frequency limit the minority carrier lifetime is shortened.

Presenting the results in different manners showed a number of differences between dark and illumination curves. Firstly, the illumination curves are a closer fit to their theoretical counterparts than dark ones in terms of semicircular fullness. Secondly, the values of impedance and dynamic resistance decreased more severely in the illuminated case as a result of applied reverse bias voltage than the dark curves. Thirdly, the dark curves at 0v and 0.2v bias voltage appear to be deviating significantly from the theoretical semicircular form. These deviations were interpreted as a result of one or more parameters of the equivalent circuit behaving as functions of frequency. Further work is needed at lower frequencies than used in this project to determine whether the semicircular form would be obtained at lower frequency, or whether the curves would continue as straight lines.

This technique was found to be very effective for interpreting the length of the minority carrier lifetime and generation rates in the i-layer of a-Si:H solar cells. Furthermore, the experiment also gave an insight into the variation of the dynamic
function of bias voltage at room temperature and constant frequency. The results from these measurements showed the effect of the photogenerated carriers on the impedance of the cell and the photogenerated voltage has shifted the complete curves to higher bias voltages corresponded to the illumination intensities.

Results from transient photocapacitance measurements for an experiment similar to that of Crandall [1982] and Qi Wang et al., [1996] were presented. This technique allowed more information to be obtained on the i-layer generation-recombination processes. The photocapacitance arising from the electric field induced displacement of photogenerated charge carriers. This photocapacitance is a measure of the space charge in shallow traps. We have demonstrated that the photocapacitance detects the net charge change in the depletion region of the device and showed that the electron and hole transitions from gap states give signals of opposite sign. In this method, the spatial region variation was examined by variation of the applied bias voltage.

Sub-bandgap energy transitions were examined for the same sample and showed a significant contribution to the quantum efficiency of the device. These results are fundamentally in good agreement with those of Vanmaekelbergh and deLagemaat [1994] and Zhou et al., [1991]. Trapping of a hole from the valence band and thermal emission of an electron from conduction band was interpreted in the similar way as these authors. From the experimental calculations of sub-bandgap energy photons it was possible to involve a cascade of photons to produce an electron/hole pair and enhance the photoconductivity of the cell. The results have also enabled us to differentiate between excitations caused by various photon energies provided by different illuminations.
6.2 Light Soaking

The results from light-induced changes in a-Si:H p-i-n solar cells were in good agreement with those found by Bolko van Roedern [1991], Dai Guo-Cai et al. [1989], and Carlson et al., [1997]. The changes in dangling bonds were interpreted in the same way as above authors. The charged dangling bonds in the i-layer of a-Si:H solar cells are formed out of neutral ones as a result of light soaking. Hence, the total number of dangling bonds in this region, which act as recombination centres, increases and reduces the electric field of the i-layer. The electric field change will redistribute the total number of space charges, that are determined by the corresponding changes in internal field. This change leads to stabilisation and determining the performance of the device.

We have interpreted the results in terms of change in cell’s parameters (fill factor, current density, and efficiency) and parameters of the equivalent circuit of the cell (dynamic resistance, capacitance, and overall impedance of the cell). Prolonged light exposure was found to reduce the fill factor by 27% of its initial value, the current density has dropped to almost a half, and the efficiency to a third after 60 hours of light soaking. The massive decrease in the current density was inferred to the increase of the recombination centres in the depletion region as a result of increase in defect number in that region.

The degradation in terms of parameters of equivalent circuit has also been assessed. For typical p-i-n a-Si:H solar cell, the results have been in accordance with theoretical calculations and literature interpretation. The dramatic reduction in the
overall impedance and dynamic resistance after the light soaking provided a good explanation of the creation of defect densities in the i-layer. These defect increases have reduced the minority carrier lifetime and photogeneration at the contacts and directly affected the performance of the cell.

6.3 Annealing

Annealing was found to restore the performance of the device after 60 minutes at 180°C. From the figures 5.22 and 5.23 it was observed that a large number of defect states in the depletion region was decreased. This decrease, however, was due to conversion of the charged dangling bonds into neutral ones as a result of temperature rise. These defect states would limit the minority carrier lifetimes in the i-layer. For the cells used in present work, the minority carrier lifetimes were found to be close to that for the as-deposited state.

The recovery of the current density and the fill factor in a-Si:H solar cells may be related to the photogenerated electrons and holes which drift to the opposite sides under build-in electric field. The excess defect states by light soaking were removed by annealing, and the saturation of the remaining defect states was easily reached.

The impedance spectroscopy measurements in the figure 5.27 has provided an explicit evidence of the performance recovery of the device. The recovery of the dynamic resistance and the impedance of the equivalent circuit, close to their initial values, were found to be associated with densities of states and minority carrier lifetime of the charged carriers in the depletion region. Hence, the electric field in
this region plays a crucial role in assessing the efficiency by displacing the thermally generated carriers to the contacts.

Results from the annealing process provided an insight into the recovery mechanism after the severe decline in performance caused by the light soaking. It was observed that both mechanisms (degradation and recovery) totally depend on the space charged dangling bonds and the minority carrier lifetimes which in turn limited the performance of this material.

6.4 Further Work

This project has shown the use of impedance spectroscopy (IS) technique in characterisation of p-i-n a-Si:H solar cell and studied the microscopic mechanisms in the i-layer that limit the performance of the cell. However, the aims of this project mostly successfully have been covered. However, because there were some that needed more facilities to be achieved they therefore remain unsolved. We recommend the following problems should be addressed in further work.

A- The temperature is one of the most important parameters in the study of hydrogenated amorphous silicon solar cells. Investigating the cell at different temperature could lead to different curves in the shape and values of impedance and dynamic resistance. These changes are decisive of limiting minority carrier lifetime and trapping/detrapping mechanisms in the i-layer of the cell. This information would enable us to produce cells with better quality and performance.
The initial measurements of the dark cell at 0v and 0.2v showed unsatisfactory results that possibly deviated from the theoretical curves by using available frequency range (20Hz-300kHz). It was argued by Cohen et al., [1982], that the temperature scale is isomorphic to a logarithmic frequency, when the dynamics are controlled by a thermally activated variable such as thermal trapping rate or the resistivity. Based on that, however, further work could be done to investigate the performance at frequencies below our minimum frequency (<20Hz). The results would allow us to observe whether the curves ultimately become semicircular in form with large radii, or continue as straight lines.

B- Although this work is a simple attempt to investigate an increase in quantum efficiency yield by sub-bandgap photons in a-Si:H solar cells, It has studied the transition possibilities. Further experimental works are needed to reveal crucial information about the minority carrier lifetime and recombination process to support the qualitative interpretation of this work (generation of electron/hole by multiple photons and a single photon transition).

The first step to be done therefore would be to develop a technique such as intensity modulated photocurrent spectroscopy (IMPS). This method would be capable of modulation of the light and provide sub-bandgap energy photons on the wider scale of the spectra that have not been done in this work. For the same samples this will determine qualitative information about fundamental mechanisms that occur through multiple photon absorption.

C- The photocapacitance measurements at room temperature and steady illumination have provided valuable information on density of states (DOS) and generation
charged carriers in the i-layer. Extension of this work with variation of temperature and illumination is expected to give crucial information about DOS and generation rate.

D- In analysing complex plane of impedance for any cell, a semicircular shape of the curve is indicative of an AC equivalent circuit consists of a capacitor with resistor in parallel. The results from electrochemical cells showed a second semicircular curve, at very high frequency, has appeared and is involved in the modelling of the cell. This is possible to be the case in a-Si:H solar cell materials as well. Therefore, further work in this range of frequency would lead to enormous information about the modelling the cell and type of processes proceed in the cell. Transport properties and minority carrier lifetime also can be found for the material.

This technique together with open circuit voltage decay (OCVD) studied by Mahan (1979) provide complementary information about type of processes and performance of p-i-n a-Si:H solar cells. Both methods have been used to investigate the degradation problem in this type of materials that was first studied by Staebler and Wronski (1977). Unfortunately, not many papers published involve using IS technique in the study of these materials. Therefore, further work using this method is needed to confirm this work and to obtain more information that could be used in practical applications.
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