4 Computer modelling of the a-Si:H solar cell device

4.1 Introduction

The application of computer modelling to study the performance of amorphous silicon solar cells has been successful in explaining properties that can not otherwise be obtained through experiments. In section 3.7.1, we mentioned the inadequacies of using experiments and analytical methods to explain the changes in internal parameters of the solar cell during light soaking. In view of these inadequacies and in order to go beyond the simple explanation of the degradation kinetics obtained in chapter 3, we shall apply computer modelling schemes to analyze a-Si:H solar cells in both the as deposited and degraded state and intermediate stages.

There are several computer programs that have been developed for modelling amorphous and microcrystalline silicon solar cells in which flexible and sophisticated models describing amorphous silicon electronic properties are implemented [13]. Most of these programs are designed to address specific problems that make modelling of amorphous silicon devices rather complex. These issues are described in details in references [13,10]. The computer simulations in this study will be realized through the use of the ASA (Amorphous Silicon Analysis) program developed at Delft University of Technology. Our work will be focussed on the analysis of the experimental results obtained from light soaking of a-Si:H solar cells. We shall investigate the contributions of different defect states to the light induced changes in the operation of a-Si:H solar cells. The degraded states will be modelled by assuming the increase of dangling bond density of states according to the model of defect creation described by Stutzmann et al [63]. The description the of Stutzmann et al model and its implementation in this study are given in section 6.2.

4.2 Transport equations

The modelling of a-Si:H solar cell requires the solution of the basic semiconductor equations which are the hole and electron continuity equations and Poisson's equation. Assuming the non existence of a magnetic field and under isothermal
conditions, the semiconductor equations are given as follows:

\[ \nabla \cdot (\varepsilon \nabla \psi) = -\rho \]  \hspace{1cm} (4.1)
\[ \frac{\partial n}{\partial t} = \frac{1}{q} \nabla \cdot \vec{J}_n + G_{opt} - R_{net} \]  \hspace{1cm} (4.2)
\[ \frac{\partial p}{\partial t} = \frac{1}{q} \nabla \cdot \vec{J}_p + G_{opt} - R_{net} \]  \hspace{1cm} (4.3)
\[ \vec{J}_n = n \mu_n \nabla \cdot E_{FN} \]  \hspace{1cm} (4.4)
\[ \vec{J}_p = -p \mu_p \nabla \cdot E_{FP} \]  \hspace{1cm} (4.5)

where \( \psi \) is the potential relative to the local vacuum level, \( \varepsilon \) is the permittivity of the semiconductor material, \( R_{net} \) is the net recombination rate, \( G_{opt} \) is the optical generation rate of electrons and holes, \( \rho \) is the space charge density, \( J_n \) and \( J_p \) are the electron and hole current densities which are controlled by the gradient in the corresponding quasi-Fermi levels of the free carriers, \( E_{FN} \) and \( E_{FP} \).

### 4.2.1 The band diagram and carrier statistics

The band diagram in thermodynamic equilibrium of the p-i-n structure is shown in Figure 4.1. This is a simplified structure with no buffer at the p/i interface. The figure shows the minimum energy (\( E_C \)) of the conduction band (CB). This energy level is related to the vacuum level \( E_0 \) by:

\[ E_C = E_0 - q \psi - \chi \]  \hspace{1cm} (4.6)

where \( \chi \) is the electron affinity. The minimum energy level (\( E_V \)) of the valence band (VB) is related to the vacuum energy level \( E_0 \) by:

\[ E_V = E_0 - q \psi - \chi - E_G \]  \hspace{1cm} (4.7)

where \( E_G \) is the band gap. For amorphous silicon \( E_G \) represents the mobility gap \( E_{mob} \). Under non-equilibrium conditions, the concentration of free carriers is described by the quasi-Fermi energy level for electrons \( E_{FN} \) and the quasi-Fermi energy for holes \( E_{FP} \). At thermal equilibrium we have these levels coincide, that is:

\[ E_F = E_{FN} = E_{FP} \]  \hspace{1cm} (4.8)

The calculation of free carrier concentrations in amorphous silicon is achieved through the Maxwell-Boltzmann approximation. This is because the quasi Fermi
levels in amorphous silicon are always separated by more than three $kT$ from their corresponding band edges. The free carrier densities are therefore approximated calculated from the following expressions:

$$n = N_C \exp \left( \frac{E_{FN} - E_C}{kT} \right) = N_C \exp \left( \frac{E_{FN} - E_0 + q\psi + \chi}{kT} \right)$$  \hspace{1cm} (4.9)$$

$$p = N_V \exp \left( \frac{E_V - E_{FP}}{kT} \right)$$

$$= N_V \exp \left( \frac{E_0 - q\psi \chi - E_G - E_{FP}}{kT} \right)$$  \hspace{1cm} (4.10)$$

where $N_C$ and $N_V$ are the effective density of states in the conduction and valence band. Making the energy of the quasi-Fermi levels for electrons ($E_{FN}$) and holes ($E_{FP}$) subjects in the equations 4.9 and 4.10 we obtain the following equations.
\begin{align*}
E_{FN} &= E_C + kT \ln \left( \frac{n}{N_C} \right) = E_0 - q\phi - \chi + kT \ln \left( \frac{n}{N_C} \right) \quad (4.11) \\
E_{FP} &= E_V + kT \ln \left( \frac{p}{N_V} \right) \\
&= E_0 - q\phi - \chi - E_G - kT \ln \left( \frac{p}{N_V} \right) \quad (4.12)
\end{align*}

### 4.2.2 Boundary Conditions

The solution of the system of semiconductor equations can be obtained in a finite domain representing the geometry of a solar cell. The electrical contacts at the back and front of a solar cell device in one-dimensional modelling form the boundary conditions for the solution of equations 4.1 - 4.5.

**Ohmic contacts**

For an ideal ohmic contact, the assumption of no space charge and thermal equilibrium concentrations of electrons and holes at the contacts can be taken. This assumption implies a non existence of a Schottky barrier and an infinite surface recombination velocities of carriers.

**Schottky contacts**

The Schottky barrier exists between a metal and semiconductor interface. The current flowing across the Schottky barrier is mostly dominated by the majority carriers and is governed by the mechanism of thermionic emission [80]. The current density for an ideal Schottky barrier \( \phi_b \) is described by the thermionic theory as:

\[
J_n = A^* T^2 exp \left( -\frac{q\phi_b}{kT} \right) \left[ exp \left( \frac{qV_a}{kT} \right) - 1 \right] \quad (4.13)
\]

where \( A^* \) is Richardson’s constant, \( V_a \) is the applied external bias voltage.
4.3 Density of states and occupation probability in a-Si:H

4.3.1 Tail states

The density of states (DOS) is important for the calculation of the electrical and optical properties of the material. The present day models for the electronic states are based on the Cohen-Fritsche-Ovshinsky model [81]. In section 1.2.1, it was mentioned that the absence of long range order in a-Si:H cause the density of states distribution at the band edges to gradually decrease into the band gap. The density of these tail states can be considered as a measure of the degree of disorder in the atomic structure of amorphous silicon. This is because the higher the degree of disorder in the atomic structure, the higher will be the density of allowed electronic states in the gap between the conduction and valence bands. The tail states are localized and carriers that fall into them get trapped and can not contribute to the electronic transport in a solar cell. The density of states function for the conduction band tail is:

\[ N_{CBT}(E) = N_{CO} \exp \left( -\frac{E}{E_{C0}} \right) \]  \hspace{1cm} (4.14)

and the DOS distribution for the valence band is

\[ N_{VBT}(E) = N_{VO} \exp \left( -\frac{E - E_{V0}}{E_{V0}} \right) \]  \hspace{1cm} (4.15)

where \( N_{V0} \) and \( N_{CO} \) are the density of tail states at the mobility band edges, \( E_{V0} \) and \( E_{CO} \) are the characteristic energy slopes of the exponential decreasing DOS function.

4.3.2 The dangling bond density of states

In section 2.2.1, we described the dangling bond states as amphoteric and that these states can occupy three different charge states. The models that describe the dangling bond density of states are the defect pool model and the standard defect model. The description of the defect pool model is well covered in section 2.2.2 and will be omitted in this section. The standard defect model of the DOS assumes a gaussian distribution of the dangling bond transition energy levels. The two gaussians shaped DOS distribution representing the transition levels \( E^{+/-0} \) and \( E^{0/-} \) with correlation energy \( U \) are defined as:
\[ N_{db}^{+/0}(E) = \frac{1}{\sigma_{db}\sqrt{2\pi}} \exp \left[ -\frac{(E - E_{db}^{+/0})^2}{2\sigma_{db}^2} \right] \]  

\[ N_{db}^{0/-}(E) = \frac{1}{\sigma_{db}\sqrt{2\pi}} \exp \left[ -\frac{(E - E_{db}^{0/-})^2}{2\sigma_{db}^2} \right] \]  

where \( N_{db}^{+/0}(E) \) is the distribution of the energy levels related to the +/0 transition, \( N_{db}^{+/0}(E) \) is the distribution related to the 0/- transition, this distribution is centred around \( E_{db}^{0/-} = E_{db}^{+/-} + U \), \( N_{db} \) is the total dangling bond density, \( E_{db}^{+/-} \) and \( E_{db}^{0/-} \) are the energy positions for the two gaussian peaks and \( \sigma_{db} \) is the width of the distribution.

Wronski et al [82] have shown that the standard model can be applied to doped a-Si:H. They found that the effect of dopants on the DOS profile in a solar cell accounts for the deep states distribution. The density of charged DB states increases exponentially as the Fermi level shifts from midgap for both n and p type amorphous silicon.

### 4.3.3 Recombination and generation statistics

We proceed with the description of the distribution of charge carriers between the valence and conduction bands and the defect levels in amorphous silicon. When a semiconductor is in thermal equilibrium, the carrier density is constant. The value of this constant can be altered by several forms of energy (e.g. optical and thermal) which can excite electrons from one state to another of higher energy, a process known as generation. The process of generation has a converse recombinative or de-generative process in which electrons undergo transitions to states of lower energy and release some form of energy. It should be understood that in thermal equilibrium, generation and recombination of carriers are constantly taking place, but on the average for every electron excited into the conduction band one recombines or drops back into the valence band. Under the assumption that the recombination centres are non-interacting the net recombination and generation (R-G) rate is calculated from [13]

\[ R_{\text{net}} = \int_{E_{V,\text{mob}}}^{E_{C,\text{mob}}} N(E) \eta_R(E) \, dE \]  

where \( N(E) \) is the density of states a function of energy in the band gap and
\( \eta_R(E) \) is the recombination efficiency of a state at energy \( E \). The trapped charge in the tail states is calculated for donor-like and acceptor-like states:

\[
\rho_D = q \int_{E_{\text{mob}}^C}^{E_{\text{mob}}^A} N_D(E)[1 - f(E)]dE \tag{4.19}
\]

\[
\rho_A = q \int_{E_{\text{mob}}^C}^{E_{\text{mob}}^A} N_A(E)f(E)dE \tag{4.20}
\]

where \( f(E) \) is the occupation function. For amphoteric dangling bond states, the space charge is given by:

\[
\rho_{DB} = q \int_{E_{\text{mob}}^C}^{E_{\text{mob}}^A} N_{DB}(E)[F^+(E) - F^-(E)]dE \tag{4.21}
\]

where \( F^+(E) \) and \( F^-(E) \) are the probability functions for the empty and doubly occupied dangling bonds, respectively.

To model the recombination and trapping mechanism in a-Si:H the Taylor and Simmons [83], 116] statistics can be applied to the Shockley-Read-Hall (SRH) model. The shockley-Read-Hall model considers recombination via a single-electron trap. The Taylor and Simmons statistics uses the SRH statistics for application to recombination problems with a continuous distribution of gap states instead of the discrete recombination levels as described by the SRH statistics. The details of SRH statistics and of the Taylor and Simmons statistics will not be covered in this thesis, we recommend the interested reader to references [13,10,83,84].

We shall instead discuss the recombination and charge trapping of amphoteric dangling bond states. Recombination and generation statistics (R-G) involving the two level representation of dangling bond states is correctly described by the Sah and Shockley multilevel R-G statistics. The possible electronic transitions between the R-G centers and the energy bands are illustrated in Figure 4.2[13]. The rates of change in carrier concentrations arising from these transitions are given in Table 4.1.

Following Street and Mott [85], each dangling bond can be occupied by zero, one or two electrons. It is considered that an electron can be captured by a \( D^+ \) or a \( D^0 \) state and a hole can be captured by a \( D^- \) or a \( D^0 \) state. The total capture rate of electrons by a \( D^+ \) and \( D^0 \) and holes by \( D^- \) and \( D^0 \) are respectively,

\[
nC_{p, n}^+, nC_{n, p}^0, pC_{p, n}^- \text{ and } pC_{p, n}^0, \]

where \( C_{n, p}^0 \) and \( C_{p, n} \) denote electron and hole capture coefficients for a given charge of dangling bond (indicated as a superscript). The capture coefficient is a product of the velocity \( (v_{th}) \) of a given carrier and the
Figure 4.2: Schematic diagram representing the capture and emission processes between the energy bands and the amphoteric the dangling bond states.

capture cross section ($\sigma$) for capture by a trap. Inverse processes of emission of an electron from a filled dangling bond into the conduction band and the emission of a hole from an empty dangling bond into a valence band are denoted by emission coefficients $e^+_n$, $e^0_n$, $e^-_p$ and $e^0_p$ respectively. The rates of capture processes and emissions are listed in Table 4.1. The probability that a dangling bond is in a positive, neutral or negative charge state is given by the occupation functions $f^+$, $f^0$ and $f^-$, respectively. The sum of the occupation functions must be equal to one. At thermal equilibrium the occupancy functions ($f^+_o$, $f^0_o$, $f^-_o$) of the different charge states of the dangling are given as follows:

$$f^+_o = \frac{1}{1 + 2\exp[(E_F - E_t)/kT] + \exp[(2E_F - E_t - U)/kT]}$$  \hspace{1cm} (4.22)

$$f^0_o = \frac{2\exp[(E_F - E_t)/kT]}{1 + 2\exp[(E_F - E_t)/kT] + \exp[(2E_F - E_t - U)/kT]}$$  \hspace{1cm} (4.23)

$$f^-_o = \frac{\exp[(2E_F - 2E_t - U)/kT]}{1 + 2\exp[(E_F - E_t)/kT] + \exp[(2E_F - E_t - U)/kT]}$$  \hspace{1cm} (4.24)

where $E_t$ is the energy of the amphoteric dangling bond state with the $+/0$ transition being at energy $E_t$ and the $0/-$ transition being at $E_t + U$.

At steady state condition the numbers of electrons and holes in the conduction and valence bands are assumed constant. The maintenance of a constant number of carriers in the band states at steady state or equilibrium conditions is governed by the principle of detailed balance, which states that under equilibrium conditions
every process and its inverse must proceed at exactly equal rates. Following this principle, at equilibrium, the capture and emission rates depicted in Figure 6.1 are assumed equal.

\[
\begin{align*}
nC_n^+ N_r f^+ &= e^0_n N_r f^0 \\
nC_n^0 N_r f^0 &= e^-_n N_r f^- \\
pC_p^- N_r f^- &= e^0_p N_r f^0 \\
pC_p^0 N_r f^0 &= e^+_p N_r f^+ 
\end{align*}
\]

(4.25)

From the above equations we can consequently determine emission coefficients as functions of capture rates for equilibrium situation.

\[
\begin{align*}
e_n^0 &= nC_n^+ f^+ / f^0 \\
e_n^- &= nC_n^0 f^0 / f^- \\
e_p^0 &= pC_p^- f^- / f^0 \\
e_p^+ &= pC_p^0 f^0 / f^+
\end{align*}
\]

(4.26)

Fractional Occupancy of different charge states of Dangling bonds during illumination

Under steady-state illumination, the system is not at equilibrium and therefore none of the equilibrium carrier concentration are valid, nor is the occupancy determined by the Fermi-Dirac distribution applicable. Instead the electron and hole densities are characterised by quasi-Fermi levels and their fractional occupancy depends on the intensity of the excitation stimulus.
In the steady-state condition, the emission deficit for electrons and holes must be equal so that the net rate of recombination is the capture rate minus the emission rate. By equating the net recombination rates of electrons and holes, the fractional non-equilibrium occupancy functions ($f_{neq}^+, f_{neq}^0, f_{neq}^-)$ of the dangling bond states under illumination can easily be calculated as shown by Vaillant and Jouse [86].

$$f_{neq}^+ = \frac{1}{1 + \frac{e_p^0 + pe_n}{e_p + nc_n}} \left[ 1 + \frac{e_p^0 + pe_n}{e_p + nc_n} \right]$$ (4.27)

$$f_{neq}^0 = \frac{1}{1 + \frac{e_p^0 + pe_n}{e_p + nc_n} + \frac{e_p^0 + pe_n}{e_n + pc_p}}$$ (4.28)

$$f_{neq}^- = 1 - f^0 - f^+$$ (4.29)

### 4.3.4 Photogeneration of carriers

The simulation of the electrical characteristics of a solar cell can be done under illuminated conditions. This means that any electrical modelling will require an auxiliary optical program for calculation of the absorption profile in a solar cell. The absorption profile is necessary for determining the generation profile of carriers in the device. Two approaches can be used to model the solar cell as an optical structure. The first involves consideration of the solar cell as an optical system with smooth interfaces. The second involves the description of the solar cell device as a structure containing one or more rough interfaces. In the section 4.1, we mentioned that the simulation program used in this study is the ASA program developed at Delft Univeristy of Technology. The ASA program has the option of using the two types of optical programs which are based on structures with smooth or rough interfaces. Of interest in this study is the use of the auxiliary optical program GENPRO II.

GENPRO II determines the generation rate profile in a solar cell from the absorption profile by taking scattering at rough interfaces into account. This approach is realistic for a-Si:H solar cells as they are deposited on randomly textured substrates as a means of increasing the efficiency through a light trapping mechanism. According to the multi-layer structure model, at every interface the intensity of light is determined as long as the intensity of incident light, the optical properties of all the media and the scattering parameters of the interfaces are known. Shown in Figure 4.3 generation profiles obtained for a multilayer structure with rough and for smooth interfaces. We observe that the generation profile from the case of rough interfaces is slightly higher than the case of smooth interfaces.
Figure 4.3: The generation profiles of a solar cell obtained for the case of smooth and rough interfaces.

4.4 Concluding remarks

We have presented the physical models for amorphous silicon and the set of equations used in the computer modelling of the a-Si:H p-i-n solar cells. The models include the description of the continuous density of states in the band gap of a-Si:H and the recombination and generation statistics of these states. A brief description of the optical models for calculating the optical generation profiles in a p-i-n structure was given. The models described in this chapter have been successfully applied by several workers to gain insight into the physics of amorphous silicon solar cells. Through the application of these models a greater insight into the physical mechanisms governing the operation amorphous silicon solar cell have been established.