6 Modelling the degradation kinetics of a-Si:H p-i-n solar cells

6.1 Introduction

In section 5.2, it was mentioned that for simulating the operation of a solar cell, a number of physical parameters and models are used in the simulation process. However the existing models in ASA do not permit simulation of a solar cell during degradation as they have no facility for describing the light-induced defect creation process. We have already mentioned that the kinetic model of Stutzmann et al (SJT) [63] is widely accepted for describing the light-induced dangling bond creation process. On the basis of this model, we have developed two computer modelling approaches for simulating the degradation kinetics of a-Si:H solar cells.

The first approach involves a direct application of the Stutzmann et al model to develop a dynamic scaling relation and fitting formula for the increase in the dangling bond density of states during light soaking. To reflect the evolution of different charge states of the dangling bond, the scaling relation which is a quasi-steady state (non-equilibrium) formulation scales the shape of the density of states with three gaussians. The initial density of states distribution is calculated by the ASA program according to the defect pool model (DPM). Using the recombination of the dangling bond states as the driving force for defect creation, an iterative scheme was designed in the ASA simulation program to track the defect density as a function of illumination time and position in the solar cell. A coefficient for the creation rate is the available fitting parameter.

The second approach uses the kinetic model of Stutzmann et al(SJT) [63] together with an annealing term. In this approach the growth of light induced dangling bonds is inhibited by an annealing process. The approach is accomplished outside the ASA program, however the initial defect profile for a given solar cell used as an input to the model is obtained from the ASA simulation. In this approach the coefficient for the creation rate to together with the annealing time are used as fitting parameters.

This chapter reviews both the formulation of the SJT model and the description of two approaches for simulating the degradation kinetics of a-Si:H solar cells. Through simulations of the experimental results, it will be shown that direct application of the SJT model without the annealing term does not reproduce the
saturated light induced defect density.

6.2 The Kinetic model of Stutzmann et al (SJT)

Stutzmann et al, 1984 proposed a kinetic model which relates the density of dangling bonds to the intensity and duration of light exposure. According to this model, light induced degradation of a-Si:H is a result of the metastable midgap defects created from weak Si-Si bonds broken by bimolecular non-radiative recombination process between the optically excited electrons and holes. In the context of this model electrons trapped in the antibonding orbital (conduction band tail) and holes trapped in the bonding orbital (valence band tail) form excitons. Recombination of these bandtail excitons release energy ($\approx 1.3eV$) which can break a weak Si-Si bond and lead to creation of new midgap defects. Since the model considers defect creation as a consequence of non-radiative recombination between optically excited electrons and holes, a good description of the excess carrier distribution during light exposure is required to understand the effect. However, as pointed out by Stutzmann et al [63], the details of carrier concentrations at high temperatures $T > 200K$ have less effect on the kinetic modelling of the SWE. At such temperatures, the life time of excited carriers is sufficiently short ($\tau < 1ms$) making it comparable to the exponential decay constant of the band tails. This means that thermal equilibration of band tail states and extended states is readily achieved. The integral densities of excited electrons ($n$) in the energy levels of the (shallow) conduction band-tail and above and that of holes ($p$) in the corresponding levels of the valence band can be expressed as

$$n = \int_{CB} f_n(E, T, G, N_r, p)N(E)dE \quad (6.1)$$

$$p = \int_{VB} f_p(E, T, G, N_r, n)N(E)dE \quad (6.2)$$

Here $N(E)$ is the electronic density of states, $f_n$ and $f_p$ are the occupation functions for electrons and holes, $T$ is the temperature, $G$ is the generation rate and $N_r$ is the density of recombination centres. For amorphous silicon, the recombination centre is given by the three different charge states of the dangling bond;

$$N_r = N^+ + N^0 + N^- \quad (6.3)$$
where \( N^+ \) and \( N^- \) are the densities of the charged dangling bond states and \( N^0 \) is the density of neutral dangling bonds.

**Free carrier transition mechanism**

To obtain the relationship between the density of recombination centres and the integral densities of excited electrons (\( n \)) and holes (\( p \)), we proceed with the description of the distribution of charge carriers between the valence, the conduction bands and the defect levels in amorphous silicon. For amorphous silicon the existence of different defect states in the band gap (as explained in chapter 2) which act as trapping and recombination levels makes the analysis of generation and recombination in this material more complex. One has to consider a whole set of possible electron and hole transitions and obtain the corresponding rate equations for the changes in occupation levels. The various types of electronic transitions available in amorphous silicon may be depicted as in Figure 6.1. Incident radiation induces optical excitation (\( G \)) of electrons from the valence to conduction band forming electron-hole pairs. The excited electrons through a process of thermalization move into shallow band tail states (\( V_{BT} \) and \( C_{BT} \)) where they are capable of taking part in the conduction by a multiple trapping mechanism. The charge states of dangling bonds are represented as \( D^+, D^0 \) and \( D^- \). The number of free charge carriers at thermal equilibrium and at quasi-steady state conditions depends on the dynamic balance between the transitions shown in Figure 6.1. The capture rate of a dangling bond state is proportional to the number of charge carriers given by Equations 6.1 and 6.2, and to the density of recombination centres. The rate of charge emission is proportional to the concentration of occupied dangling bond states. During degradation of a solar cell, constant illumination and temperature conditions in open circuit conditions of a solar cell are applied. This means that the excess charge carriers due to illumination are not removed by an external circuit but rather allowed to decay by recombination processes in the cell. Since temperature and illumination are maintained constant for long periods, steady state conditions in the solar cells are achieved, where the numbers of electrons and holes in the conduction and valence bands are assumed to be 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. Detailed balance will in general not hold for a system which is in a steady non-equilibrium state, however in the case of a solar cell the existence of a steady-state condition together with microscopic reversible processes of capture and emission of charge carries implies the existence of detailed balance. Following this principle, at equilibrium the capture and emission rates depicted in
The recombination transitions in a-Si:H are assumed equal. According to Stutzmann et al [63], the dynamic situation in the model described by Figure 6.1 independent of the type of transition is characterized by the following rate equations:

\[ \frac{dn}{dt} = G - n(C_{n}^{0}N^{0} + C_{n}^{+}N^{+} + C_{t}p) \]  (6.4)

\[ \frac{dp}{dt} = G - p(C_{p}^{0}N^{0} + C_{p}^{-}N^{-} + C_{t}n) \]  (6.5)

\[ \frac{dN^{-}}{dt} = nC_{n}^{0}N^{0} - pC_{p}^{-}N^{-} \]  (6.6)

\[ \frac{dN^{+}}{dt} = pC_{p}^{0}N^{0} - nC_{n}^{+}N^{+} \]  (6.7)

\[ \frac{dN^{0}}{dt} = n(C_{n}^{+}N^{+} - C_{n}^{0}N^{0}) + p(C_{p}^{-}N^{-} - C_{p}^{0}N^{0}) \]  (6.8)

where \( G \) is the generation rate in \( m^{-3}s^{-1} \), \( C_{t} \) (m\(^3\)s\(^{-1}\)) is the capture rate constant for the tail-to-tail transition, \( C_{n} \) and \( C_{p} \) (m\(^3\)s\(^{-1}\)) are the capture rate constants for electrons and holes in dangling bond states. In solving the above rate equations, Stutzmann et al assumed that under a constant generation rate \( G \), the equilibration between the different occupancies in quasi-steady-state is not disturbed by the slowly increasing number of dangling bonds and therefore the distinction between the different dangling-bond charge states \( D^{+}, D^{0} \) and \( D^{-} \) can be omitted leading...
to

\[
\frac{dn}{dt} = G - n(C_n N_r + C_t p) \quad (6.9)
\]

\[
\frac{dp}{dt} = G - p(C_p N_r + C_t n) \quad (6.10)
\]

Where \(C_n N_r = C_n^0 N^0 + C_n^+ N^+\) and \(C_p N_r = C_p^0 N^0 + C_p^- N^-\) are the effective capture rates for excess charge carriers being trapped by dangling bonds of all possible charge states. After a series of manipulations involving appropriate expressions for \(n\) and \(p\) and based on the assumption that new metastable dangling bonds are created by a fraction of non-radiative, direct tail-to-tail recombination, Stutzmann et al [63] arrived at the following equation for the increase in dangling bond density of states \(N_r\) during illumination:

\[
\frac{dN_r}{dt} = C_{sw} C_t n p \quad (6.11)
\]

where \(C_{sw}\) is the coefficient for the creation rate of new dangling bonds and \(C_t\) \(\text{(m}^3\text{s}^{-1})\) is the rate of tail-to-tail recombination.

Using the following expressions for electrons and holes

\[
n = \frac{G}{C_n N_r} \quad (6.12)
\]

\[
p = \frac{G}{C_p N_r} \quad (6.13)
\]

and inserting equation 6.12 into 6.11 yields

\[
\frac{dN_r}{dt} = \frac{C_{sw} C_t G}{C_n C_p N_r^2} \quad (6.14)
\]

Equation 6.14 can be integrated to give

\[
N_r^3(t) - N_r^3(0) = 3C_{SW} \frac{C_t G^2 t}{C_n C_p} \quad (6.15)
\]

For a long duration of illumination it can be considered that \(N_r(t) \gg N_r(0)\) and equation 6.15 is simplified as:

\[
N_r(t) = [3C_{SW} C_t / C_n C_p]^{1/3} G^{2/3} t^{1/3} \quad (6.16)
\]
6.3 Degradation model using scaling relation based on SJT formulation without an annealing term.

A major consideration in this study is to show how the increase of dangling bond density of states during light exposure of a solar cell affects the output characteristics of a solar cell. In this section we derive a dynamic scaling relation that can scale a given defect density distribution according to the SJT formulation described in the preceding section. We begin with the description of the scaling factors which are applied to a given dangling bond density of states. Our interest is the scaling of the as grown defect distribution calculated according to the defect pool model. This approach enables us to estimate the contributions of the different gap states to the degradation kinetics of a solar cell. The scaling approach is verified against the experimental degradation data of a solar cell. It will be shown that apart from the differences in the saturation levels between the experimental and simulated data, the overall prediction of the model closely describe the experimentally observed features of the Staebler-Wronski effect.

6.3.1 The scaling relationship

The dynamic scaling relation for the increase in the dangling bond density of states based on the SJT kinetic model is obtained by diving both sides of equation 6.15 by \( N_r(0) \) which is the as-deposited defect density.

\[
\frac{N_r(t)}{N_r(0)} = 1 + \left[ \frac{3C_{SW}C_t}{C_nC_p} \right]^{1/3} G^{2/3} t^{1/3} \frac{1}{N_r(0)}
\]  

(6.17)

Letting the ratio \( N_r(t)/N_r(0) = k(t) \), replacing the generation rate (G) with the dangling bond mediated recombination rate (R) (in m\(^{-3}\)s\(^{-1}\)) and introducing a prefactor:

\[
C_{LS} = \left( \frac{3C_{SW}C_t/(C_nC_p)}{N_r(0)} \right)^{1/3}
\]  

(6.18)

leads to a dimensionless scaling factor \( k \).

\[
k(t) = 1 + C_{LS} R^{2/3} t^{1/3}
\]  

(6.19)

The scaling factor determines the increase in the defect density at a given time \( t \) (in seconds). At \( t = 0 \), \( k = 1 \) implying that the number of recombination
centres is equal to the as-deposited defect density $N_r(0)$ and the change in this number is determined by the changes in the last term of equation 6.19. In this work we assume that the capture rate coefficients for the different charge states of the dangling bond remain constant during light soaking. Thus the value of $C_{LS}R^{2/3}t^{1/3}$ as a function of light soaking time is dependent on the value of $C_{sw}$ which is the coefficient for the creation rate of new dangling bonds. The following values of the capture rate coefficients deduced from literature [63] have been used in our simulations.

\[
\begin{align*}
C_t &= 3.0 \times 10^{-17} (m^3 s^{-1}) \\
C_n &= 12.0 \times 10^{-15} (m^3 s^{-1}) \\
C_p &= 2.7 \times 10^{-15} (m^3 s^{-1})
\end{align*}
\]

The scaling factors for different dangling bond states during degradation

We can calculate the dangling bond density of states distribution for the as-deposited state of a solar cell as a function of energy, position and time ($N_{db}(E, x, t(0))$) using the defect pool model (see Figure 5.3) and from it the ASA program calculates the recombination rate $R(x, t(0))$. The light-induced defect creation is not described by the defect pool model but rather by the defect kinetic equation 6.11. Since it is known from ESR experiments that the increase in the neutral dangling bonds during light soaking is not the same as its charged counterparts, to describe the defect creation process in a-Si:H, requires different creation rates for the different charge states of the dangling bond. This behaviour can be illustrated by assigning different values of $C_{sw}$ for different charge states of the dangling bond during light soaking. Based on equation 6.19 we introduced the scaling factors $k_e$, $k_h$ and $k_z$ with different values of $C_{sw}$ to simulate the degraded state of a cell. These factors correspond to dangling bond states $D_e$, $D_h$ and $D_z$ respectively. The predictions of various calculations based on the defect pool model show that the ratio of charged-to-neutral defects at equilibrium (in the as deposited state) is between three and seven [95], by light soaking the solar cell, this ratio drops to one. Based on this prediction, the scaling factors for individual charge states of the dangling bond can be altered through the fitting parameters $C_{sw}$ to fit the experimental data.

Significance of the recombination rate in the degradation model

Since the recombination process is the main driving force for light induced defect creation process in a-Si:H, in this section we first give a brief summary of the recombination mechanism. This will provide the necessary background for
describing the procedures involved in executing the degradation model. Recombination mechanisms in a-Si:H have been extensively studied using different techniques such as electron spin resonance (ERS) [96], light induced electron spin resonance (LESR) [97,98], optically detected magnetic resonance (ODMR) [99], photoluminescence (PL) and photoconductivity (PC) [98]. It is now clear that the band-tail and dangling bond states play a major contribution to the recombination dynamics. Furthermore, it has been established through these experiments that recombination in a-Si:H is either radiative or non-radiative. Detailed explanation of these two recombination processes is well covered in reference [6].

Accordingly, the defect creation model of Stutzmann et al assumes that electrons trapped in the antibonding orbital (conduction band tail) and holes trapped in bonding orbital (valence band tail) of the same weak Si-Si bond form excitons. Experimental support of this model is given in the paper of Brandt et al [100]. Following the results of optically detected magnetic resonance (ODMR) at low temperatures [101,102] there is no reason to doubt the existence of excitons in amorphous silicon. However, the details of how non-radiative recombination of such an exciton happen is still not clear. It is generally believed that most of the exciton recombination is radiative, though non-radiative recombination is also possible. Photoluminescence experiments on a-Si:H material, have shown that, the PL intensity decreases very rapidly as the spin density is increased [103]. This observation demonstrates that dangling bonds are non-radiative centers. On the other hand luminescence has been observed to exhibit maximum intensity in a material with the lowest defect density, implying a process associated with transitions between band-tails. Such results discount the non-radiative nature of tail-to-tail transitions. In spite of this, there have been experimental observations where exciton localization in the band tails of a-Si:H have been identified to contribute to both radiative and non-radiative recombination. For example, light induced electron spin resonance (LESR) [97,98], has identified resonances at \( g = 2.004 \) and \( g \cong 2.013 \) as electron and hole band-tails. In a later experiment, Street et al [96] using ODMR on low-defect a-Si:H identified resonances corresponding to radiative and non-radiative recombination of electron and hole band-tail states. These results confirm the existence of non-radiative recombination and it is a fraction of these recombinations that create new metastable dangling bonds.

In the ASA program, the recombination and generation (R-G) rate (in m^{-3}s^{-1}) of all states in the band gap is calculated as a sum of the net R-G rates of the valence and conduction band tails and the dangling bond states. The ASA program computes the following recombination rates:

1. Total recombination \( R_T(x,t) \)
2. Recombination through CB tail states $R_{CB}(x,t)$

3. Recombination through VB tail states $R_{VB}(x,t)$

Since the tail to tail recombination is not available in the ASA program calculation, we investigated as will be shown later, the effect of using the total recombination rate and also the recombination rate through valence band tail states to calculate the k-factors (Formula 6.19). Through computer simulations we established that the recombination rate through the conduction band tail states is very small. Actually, the simulations showed that the overall sum of the recombination rates through the tail states is dominated by the VB tail states recombination. Thus, recombination through CB tail states will have almost no effect in driving the defect increase. The recombination rates calculated by the ASA program is given as a function of position in the solar cell and time $R(x,t)$. Shown in Figure 6.2 is the recombination profile through valence band states, the total recombination and the generation profile used for our simulations.

The computation procedure

In this section we shall describe the procedure for simulating the degradation kinetics of a-Si:H solar cell using the dynamic scaling relations described in the preceding sections. The implicit iterative structure for increasing the dangling bond
density of states in a solar cell at a given time \( t_i \) is shown in the flow chart of Figure 6.3. The part of the flow chart denoted as ASA depicts the simulations that the ASA program accomplishes. The overall procedure begins with the calculation of the as deposited dangling bond density of states distribution according to the defect pool model. The output of this calculation is shown in box 1 as \( N_{db}(E,x,t_i) \), implying that the defect density is calculated as a function of energy, position in the solar cell and time (the subscript zero indicates the as deposited condition at \( t=0 \)). The ASA program then uses the defect density \( N_{db}(E,x,t_i) \) to calculate the recombination profile \( (R(x,t_i)) \) of box 2 at the \( i^{th} \) light soaking time. In the as deposited state, the ASA program utilizes the defect density of box 1. The part of the flow chart outside the one denoted as ASA is used for calculating the scaling factors and the dangling bond density of states according to SJT model. Box 3 generates the k-factors \( (k_e, k_h, k_z) \) using the formula \( k_{e,h,z}(x,t_i) = k_0 + F_{STJ}(R(x,t_i))/C_{LS}R^2/3^1/3 \). The k-factors are then fed into box 4 for calculating the defect density \( N_{db}(E,x,t_i) \) at the \( i^{th} \) time using the formula \( N_{db}(E,x,t_i) = k_{e,h,z}(x,t_i)N_{db}(E,x,t_{i-1}) \). The new defect density from box 4 is then fed into the ASA program (box 2) and used to calculate the new solar cell parameters and new recombination profile. This procedure continues iteratively utilizing the recombination file \( R(x,t_{i-1}) \) to calculate the k-factors at \( i^{th} \) time which are then used iteratively to scale the previously calculated defect density in accordance with the SJT model. The procedure continues for a given period of time corresponding to the light soaking time.

6.3.2 Results of the simulations

In this section we shall present the results of the simulation exercises which were conducted to test the effect of the scaling factors on the degradation kinetics of a solar cell. In obtaining these results we considered an increase in both the charged \( D^+ \) and \( D^- \) and neutral \( D^0 \) dangling bond states and a decrease in the ratio of charged-to-neutral dangling bond states during light soaking. The appropriate recombination rate used for driving the defect increase was determined through the simulation procedures.

1. The evolution of the k-factors

We begin by showing the variation of the k-factor with time. Shown in Figure 6.4 is the inverse of the scaling factor as a function of equivalent light soaking time for \( C_{sw} = 1 \times 10^{-7} \). The two curves were obtained using the total recombination rate \( R_T(x,t) \) and the recombination rate \( R_{VB}(x,t) \) through the valence band tail states. It is observed that for the same value of \( C_{sw} \), the k-factor decays more rapidly when the total recombination is used.
in the calculation. This prompted us to use the recombination through the valence band tail states for all our simulations. The increase in the k-factor is inversely proportional to the fill factor of the solar cell and its dependence on time reflects the evolution of the fill factor during light soaking. It should be realized that the increase in defect density for simulating the degradation kinetics of a cell is determined by the evolution of the k-factor and that the saturation of the k-factor reflects the saturation in the defect density.

2. Influence of \(C_{sw}\) on the degradation curve

Our next exercise is to study the effect of varying the coefficient for the creation dangling bond states \(C_{sw}\) on the output parameters of a solar cell. Four values of \(C_{sw}\) listed below were used for this study and the program was let to run for an equivalent light soaking time of \(1.0 \times 10^9\) seconds.

(a) \(C_{sw} = 1.0 \times 10^{-5}\)

(b) \(C_{sw} = 1.0 \times 10^{-6}\)
The evolution of the inverse of the k-factor with light soaking time.

(c) $C_{sw} = 1.0 \times 10^{-7}$

(d) $C_{sw} = 1.0 \times 10^{-8}$

The changes in the degradation curve arising from different values of $C_{sw}$ are shown in Figure 6.5. Though it is observed that the experimental curve is approximately fitted when $C_{sw} = 1.0 \times 10^{-7}$, we notice that the time at which saturation is achieved is different for experimental and simulated curves. This behavior demands further investigation, as saturation can be a result of the balance between the annealing and defect creation mechanism or can be due to the complete shunting of the recombination path that drives the defect creation. The issue of saturation of the defect density has been extensively investigated by many groups and appropriate models have been suggested [104,44,105]. Based on the work of Redhill et al [104], we shall in section 6.4 show that the growth of the concentration of dangling bonds is inhibited by the annealing process.

3. **The effect of $C_{sw}$ on defect density as a function of position.**

The spatial dependence of $C_{sw}$ in the solar cell can be deduced by obtaining the defect density profile for different values of $C_{sw}$ at different light soaking times, this dependence is shown in Figure 6.6. Note that the increase
in the value of $C_{sw}$ generates more defects with higher concentrations on the p-layer side. The defect increase is minimal and almost uniformly distributed when the smallest value of $C_{sw} = 1.0 \times 10^{-8}$ was used as an input parameter. A remarkable observation is obtained from the defect profiles generated with $C_{sw} = 1.0 \times 10^{-7}$ which provided the best fit to experimental degradation curve. Accordingly, this value means that the efficiency of creating new dangling bonds ($C_{sw}$) arising from the recombination is in the orders of $1.0 \times 10^{-7}$. It implies that for every $1.0 \times 10^7$ recombinations only one such recombination leads to the creation of a new dangling bond state. A different value of $C_{sw}$ is quoted in the work of Stutzmann et al [63]. The difference implies that the efficiency of creating new dangling bond states may be depended among other factors on deposition conditions too. We also note a high rate of defect increase in the middle of the cell with increase in time of light soaking. This observation is consistent with

Figure 6.5: Comparison of the evolution of the fill factor with light soaking time for different values of $C_{sw}$
the widely observed bulk contribution to the degradation kinetics of a solar cell. The results imply that the coefficient for the creation of new dangling bonds $C_{sw}$ is position dependent in the solar cell structure. Therefore, with this approach one can obtain the correct interpretation of the degradation kinetics in a solar cell by using $C_{sw}$ as a fitting parameter. However, it should be realized that this approach does not account for the experimentally observed saturation effects in cell performance under prolonged light soaking.

![Graph showing the spatial effect of $C_{sw}$ on defect density at different stages of light soaking](image)

Figure 6.6: The spatial effect of $C_{sw}$ on defect density at different stages of light soaking

The major contribution to the degradation mechanism arises due to the bulk recombination. We show in Figure 6.7 the total and VB mediated recombination rate profiles obtained with $C_{sw} = 1.0 \times 10^{-7}$. Note that the recombination rate in the bulk of the solar cell increases with increase in light soaking time. The density of states distribution used for the fit at different stages of light soaking with $C_{sw} = 1.0 \times 10^{-7}$ is shown in Figure 6.8.
The results predict a larger increase of neutral than charged dangling bond states.

![Figure 6.7: Changes in the recombination profiles for different stages of degradation](image)

4. The integrated defect density as a function of time Shown in Figure 4 is the changes in the defect density profiles for different stages of degradation. These were obtained with the $C_{sw} = 10^{-7}$. With prolonged light soaking, it is observed that the increase in the concentration of dangling bonds in the middle of the solar cell is more pronounced.

In the context of equation 6.16, the increase in defect density is proportional to the cube root of illumination. We therefore calculated the integrated defect density of the solar cell for the period of illumination. Figure 6.10 shows that the integrated defect density over the duration of illumination approximately exhibits the $t^{1/3}$ dependence.

6.3.3 Conclusions

In summary we have developed a technique for modelling the degradation kinetics of a-Si:H solar cells. The technique is based on the defect creation model of Stutzmann et al [63]. It uses scaling factors to increase the different charge states of the dangling bond during light soaking. From the simulation results it has been established that the constant $C_{sw}$, which describes the average efficiency for the creation of metastable dangling bond states is position dependent in the solar cell structure. We have shown that through this approach it is possible to take into account the contributions of different charge states of the dangling bond during the degradation process.
6.4 Modelling the degradation using the SJT kinetic model with an annealing term

The SJT model just as most other defect kinetic analysis models considers thermal annealing which can remove the metastable defects at elevated temperatures. However in the actual SJT treatment, thermal annealing is negligible during the times of observation at room temperature. It is for this reason that the annealing term is lacking from the rate equation 6.11. In the preceding section, the results we obtained by direct application of the SJT model without an annealing term give saturation of the metastable defect density much later than the experimentally observed saturation. We proceed in this section with modelling the degradation of a-Si:H solar cell by introducing an annealing term in the SJT formulation.
Figure 6.9: Changes in the defect density profiles for different stages of degradation from the model without an annealing term.

Figure 6.10: The increase in dangling bond density of states during light soaking

In the preceding section, we considered defect creation in the solar cell as governed by the Stutzmann et al [63] equation:

$$\frac{dN_r(t, x)}{dt} = \text{const} n(t, x)p(t, x)$$  \hspace{1cm} (6.20)

where $N_r$ is the concentration of dangling bonds, $t$ is the time, $x$ is the position in the solar cell, $n$ is the concentration of electrons localized on tail states below the conduction mobility edge, and $p$ is the concentration of holes localized on the tail
states above the valence mobility edge. According to formula 6.14, the average concentration increases as follows

$$\frac{dN_r}{dt} = \frac{C_{st}}{N_r^2}$$ (6.21)

where

$$C_{st} = \frac{C_{sw} C_t G^2}{C_r C_p}$$ (6.22)

The growth of the concentration of dangling bonds should sooner or later be inhibited by the annealing process, which is simply described by equation 6.11 with an annealing term.

$$\frac{dN_r}{dt} = \frac{C_{st}}{N_r^2} - \frac{N_r}{\tau}$$ (6.23)

where $\tau$ is a phenomenologically introduced annealing time. Equation 6.23 can be solved analytically to give:

$$N_r(t) = N_{rs} \left\{ 1 - \left[ 1 - \left( \frac{N_r(0)}{N_{rs}} \right)^3 \right] exp \left( -\frac{3t}{\tau} \right) \right\}^{1/3}$$ (6.24)

where

$$N_{rs} = (C_{st} \tau)^{1/3}$$ (6.25)

Equation 6.24 allows us to compute the time evolution of the defect density profile. In this calculation, parameters $C_{sw}$ and $\tau$ are the adjustable parameters for fitting the experimental data.

**Implementation**

The model described above was implemented in three stages:

1. The first stage involved the calculation of the as deposited defect profile by the ASA program.
2. The second stage involved the use of the as deposited defect profile to compute the defect profiles at different stages of illuminating a solar cell. The procedure was done outside the ASA program.

3. The third and last stage involved the use of the defect profiles calculated in the second stage to simulate the degradation kinetics of a solar cell through the ASA program.

### 6.4.1 Results and discussion

Shown in Figure 6.11 are the results obtained from the two models. A same value of the constant $C_{sw}$ of $1.0 \times 10^{-7}$ was used for both model. The annealing time for fitting the experimental data was extracted from the experimental degradation curve. It is observed that the model with an annealing term produces the best fit of the experimental curve. This may imply that the saturation behaviour in a solar cell may occur due to attainment of steady state between generation and annealing.

Figure 6.11: Calculated fill factor as function of illumination as obtained from the degradation models with and without an annealing term. The curves are fitted to the experimental curve.

Figure 6.4.1 represents the evolution of the defect profiles for different stages of light soaking. The major difference with profiles obtained from the model
without an annealing term is that the model with an annealing term displays uniform increase in the concentration of defects across the cell, while the other model shows that the defect increase is non uniform across the solar cell and more pronounced in the middle of the cell. We also note that, towards saturation, the rate of defect increase reduces for the model with an annealing term.

Figure 6.12: Changes in the defect density profiles for different stages of degradation obtained from the model with an annealing term

Significance of the two approaches for studying the degradation kinetics

A combination of the two degradation models described in preceding sections is important in understanding the three aspects of light induced degradation in a solar cell. The three aspects can be described using the dependence of the fill factor on light soaking time shown in Figure 6.13. For simplicity we have divided the curve into three different regions. The initial stage (I) is a slow and in some cells almost constant regime for a long time. It defines the aspect of the solar cell before the onset of degradation. The second (II) stage defines the degradation rate of a solar cell. The third (III) and last stage defines the stabilized steady state of the solar cell. Detailed understanding of the three stages in the degradation kinetics of amorphous silicon solar cells is the way by which prediction of the degradation kinetics of the cell can be easily accomplished.

This implies that the understanding of the Staebler Wronski effect in a solar cell requires the understanding of the behaviour of the solar cell at every
stage of Figure 6.13. The model without an annealing term using the k-factors would be useful to investigate the degradation aspects of the solar cell for stages (I) and (II). This model has the advantage of using input parameters that define the microscopic processes in a solar cell such as capture rates and recombination rates. Moreover the model provides a new approach for simulating the degradation kinetics of a-Si:H solar cells by predicting the contributions of various charge states of the dangling bond to the degradation mechanism as shown in Figure 6.8. Through this model, the movement of the Fermi level as a consequence of defect increase can be deduced from the redistribution of dangling bond density of states. The second model defines the saturation behaviour in a solar cell, however it can not distinguish whether saturation occurs either due to the annealing process or depletion of the available defects or due to shunting of the bimolecular recombination process by the mono-molecular recombination. Regardless of this, it is clear that an annealing term in the SJT model is necessary to achieve saturation.
6.5 Conclusions and perspectives for further studies of the metastability of amorphous silicon solar cells

In this chapter we have given a summary description of the formulation of the Stutzmann et al [63] defect creation model and the two methods based on this model which can be used to simulate the degradation kinetics of a-Si:H solar cells. It has been shown that the method which scales the defect density as a function of energy, position in the solar cell and illumination time is useful for understanding the role played by the different charge states of the dangling bond during the degradation mechanism. The defect distribution obtained from this model was found to be in excellent agreement with the works of Schumm [37] and Stiebig et al [95] in that the increase in the density of neutral dangling bonds under illumination is greater than that of charged dangling bond states. Through simulations of the experimental results, it has been shown that direct application of the Stutzmann et al [63] model without the annealing term does not reproduce the saturated light induced defect density. For this reason we have used the model with an annealing term and obtained the experimentally observed saturation behaviour. However the question of the saturation mechanism in cell performance can not be fully answered by the annealing term. Therefore further improvement in the model is required to incorporate the terms that can distinguish whether saturation occurs either due to thermal annealing process or depletion of the available defects or due to shunting of the tail-to-tail recombination process by the recombination through midgap states. Once the saturation behaviour is well understood and explained, our approach can be useful to describe the three aspects of light induced degradation in a solar cell. Finally the methods developed here can be applied to analyze the differences in the degradation kinetics of different types of solar cells.