2 Metastability of hydrogenated amorphous silicon

2.1 Introduction

The subject of metastability in amorphous silicon goes back to the report of Staebler and Wronski in 1977 [1]. According to this report prolonged exposure to light could induce large reversible conductivity changes in amorphous silicon. The changes are reversible through thermal annealing of the sample at temperatures above 150°C. The light induced changes are now referred to as Staebler-Wronski effect (SWE). Although Staebler and Wronski did not develop a concise explanation of this effect, they made speculations that the effect of illumination leads to the increase in the density of gap states in amorphous silicon. They assumed that the new gap states resulted in shorter electron life times, producing the observed lowering of the photo conductivity. The increase in the gap states moved the Fermi level away from the mobility edge for electrons, leading to a low dark conductivity and a high activation energy. A specific mechanisms by which light can introduce gap states were not clear to them but they speculated on a possible cause of the degradation. They assumed that a localized defect undergoes a metastable structural change when it traps or acts as a recombination centre for photogenerated charge carriers. The observation by Staebler et al initiated a variety of experiments on degradation mechanism in amorphous silicon by several groups world-wide. In the next two sections we shall give a review of experimental methods that have been applied to study the Staebler-Wronski effect. The review will provide the necessary background for the approach we have taken in studying metastability of a-Si:H solar cells in this thesis.

2.1.1 Direct experimental evidence of increase in defect density upon light exposure of a-Si:H

Since the discovery of the SWE, research of metastability of amorphous silicon has followed several avenues. The early investigations were mostly directed toward the understanding of the reversible conductivity changes in this material. The work of Pankove et al [15] is among the earliest research that provided the direct evidence of the increase in defect density due to illumination. Through luminescence spectroscopy they studied the reversible light-induced changes in
Chapter 2

a-Si:H and found that illumination of a-Si:H by a laser produces recombination centres some of which are radiative in nature. They conducted the temperature dependence of the light-induced effects and observed that changes in the luminescence intensity decrease at temperatures above 100°C and explained this as an effect due to a simultaneous annealing process. Pankove et al advanced the idea that breaking of the so-called weak Si-Si bonds by light is responsible for the Staebler-Wronski effect. According to their speculation the bond breaking creates dangling bonds which can be reconstructed by thermal annealing.

Later experiments by Dersch et al (1980) [16] using Electron Spin Resonance (ESR) on undoped a-Si:H provided more specific evidence and offered structural information about defects in amorphous silicon. From their ESR experiments it has been established that all forms of a-Si:H have a paramagnetic defect with its resonance at a g-value of 2.005. They observed that an annealed sample produced the ESR spectrum with the known g-value of 2.005 and a corresponding spin density of $N_s = 9.1 \times 10^{22} m^{-3}$. Upon illumination of the sample the g-value and the line width of the spectrum remained the same but an increase in the intensity of the line by a factor of 2 was observed. The spin density after illumination rose to $N_s = 1.8 \times 10^{23} m^{-3}$. A further annealing of the sample in the dark at 200°C decreased the spin density. Dersch et al further conducted ESR experiments by hydrogen effusion and obtained the same g-value. Based on the similarity of the illumination induced ESR signal with that obtained by hydrogen effusion they explained the creation of light-induced dangling bonds by a model where Si:H bonds are broken and where by interstitial diffusion of the related hydrogen atoms sufficiently far away from these sites, metastable dangling bonds get created. They speculated that since the Si:H bonding states lie about 5 eV deep in the valence band, excitation of electrons from these states cannot be the reason for bond breaking. They assumed that non-radiative recombination of carriers photo excited in the Si-Si bonds provide sufficient energy which can be transferred to the Si-H bond. Dersch et al further advanced a model where the weak Si-Si bonds break and the neighboring Si-H bond hydrogen atoms switch over to the arising bonds, leaving dangling bonds with a somewhat larger distance from each other. As will be seen later in this thesis, these observations and speculations laid the foundation for the several microscopic models on metastable defect formation in amorphous silicon.

Other experiments that provided direct evidence for the creation and annealing of defects in a-Si:H are the changes in the field-effect density of states [17] and the reversible photo induced changes in a-Si:H using deep level transient spectroscopy (DLTS) [18].
2.1.2  Indirect experimental evidence of increase in defect density upon light exposure of a-Si:H

Indirect evidence of the reversible changes in the electronic behaviour of amorphous silicon has been obtained from reversible changes in the transport properties of a-Si:H diodes and solar cells. Staebler et al. [19] conducted experiments on Schottky-barrier diodes and observed that both the dark conductivity and photoconductivity of the diodes change upon optical exposure. Jouse et al. [20,21] studied the evolution of the electrical characteristics of a-Si:H Schottky diodes using I-V versus temperature, capacitance-voltage versus frequency and I-V under illumination. They observed a reversible light-induced bulk effect and an increase in the midgap density of states as obtained from the capacitance voltage method. Dresner et al. [22] conducted direct measurements of diffusion length in a-Si:H using the surface photo-voltage method. From the results of their experiments they demonstrated that prolonged illumination decreases the diffusion length and subsequent annealing restores the original value. In a later experiment Staebler et al. [23] studied the stability of n-i-p amorphous silicon solar cells and observed a decrease in the current density, the fill factor and the spectral response upon prolonged exposure of the cells to light. They concluded that the degradation was due to the decrease in the collection efficiency of the carriers. They assumed that the light induced changes occur in the intrinsic layer of the solar cell due to trapping and recombination of the optically generated carriers. Street [24] studied the effect of light soaking on transport and trapping of electrons and holes using the time-of-flight method. He identified the effect of light soaking on transport properties of a-Si:H as a result of the increase in dangling bond density and provided a quantitative measurements of the mobility-lifetime product (\(\mu\tau\)). The \(\mu\tau\) product decreased by an order of magnitude or more upon light soaking. Though several other methods exist for studying the reversible light induced changes in amorphous silicon, it is worth mentioning the work of Han and Fritzsche [25] who used single and dual-beam photoconductivity to investigate the light induced creation and annealing of defects in a-Si:H. In this work they obtained a different responses of the photoconductive properties of a-Si:H to light exposure and to thermal annealing and assumed the existence of two kinds of metastable defect states in a-Si:H. One kind was supposed to decrease the mobility lifetime while the other increases the sub-band gap absorption.

It is apparent that most of the experiments link the SWE to the reversible changes in the gap-state density. The conclusions arising from different workers in the study of metastability agree in principle that illumination leads to the creation of additional metastable defects in the gap. These defects act as recombination and trapping centres of the optically excited carriers. The experiments conducted on...
transport properties of amorphous silicon solar cells show that the recombination of excess carriers is responsible for the creation of metastable defects.

2.2 Metastable defect formation

Besides the creation of metastable defects in a-Si:H through illumination, other methods such as quenching of the material from high temperature, keV -electron irradiation, charge accumulation at interfaces, doping, electric current etc can induce metastable defect creation processes. It is now widely acknowledged that the phenomenon of defect creation (reactions) in a-Si:H are best described by the following processes\[6\]:

1. **The kinetics of defect reactions**

   The kinetics of defect reactions are described by a relaxation time $\tau_R$ required for the structure to overcome the bonding constraints. The relaxation time $\tau_R$ is associated with the energy barrier $E_B$ depicted by the configuration-coordinate diagram in Figure 2.1 which arises from the bonding energies. The lower energy $E_0$ in this figure represents the fully coordinated network while the higher energy $E_1$ represents a dangling bond defect. The energy difference between $E_1$ and $E_0$ is the defect formation energy. A larger $E_B$ requires a high temperature to bring the system to equilibrium in a given fixed time. The kind of defect reaction described by the energy barrier $E_B$ exhibits a high temperature equilibrium and a low temperature frozen state.

   \[
   \tau_R = \omega_0^{-1}\exp(E_B/kT) \tag{2.1}
   \]

   Calculations of the freeze-in temperature using equation 2.1 have been accomplished by equating it to the cooling rate $dT/d\tau_R$. It has been found that an energy barrier of 1-1.5 eV is required for a freeze-in temperature of 227\(^\circ\)C in case of a-Si:H [6]. The equilibration time is fairly small at deposition temperatures of (200 - 300)\(^\circ\)C with $\tau = 0.1 - 100$ s [6]. At room temperature the equilibration time is larger than a year. This means that the defects can remain in the material even when the creation source is removed. The defects can be annihilated by annealing at elevated temperatures.

2. **Chemical equilibrium processes**
Chemical equilibrium is calculated from formation energies of various states by minimizing the Gibbs free energy:

\[ G = H - TS \]  
\[ H = U - PV \]

where \( H \) is the enthalpy, \( S \) is the entropy, \( T \) is the temperature, \( U \) is the defect formation energy, \( P \) and \( V \) are pressure and volume of the system respectively. When an extra defect is added to the a-Si:H material, an extra free energy of the system (the chemical potential) is introduced and the change in the Gibbs free energy is given by:

\[ dG = -SdT + VdP + \sum_i \mu_i dn_i \]

At thermodynamic equilibrium \( dG \equiv 0 \) and the sample temperature is everywhere the same while the number of moles of each species in the sample remains constant. When this happens the first term of Equation 2.4 will
be zero. Physically the sample volume is fixed and therefore if there is no work being done on or by the sample the second term of Equation 2.4 will also be equal to zero. The third term will vary according to changes in the concentration of species towards equilibrium. The changes are governed by the chemical processes taking place in the sample through conversion of the species to other species. Generally, these rates are small so that the thermodynamic equilibrium ($dG \rightarrow 0$) is limited by the rate of the chemical equilibration among the species ($\sum_i dn \rightarrow 0$) [26]. Because of the random nature of the a-Si:H network, the formation energy is non uniform in the entire network but rather varies from site to site. This makes the evaluation of the equilibrium state in a-Si:H rather complex. A correct evaluation should include the distribution of the formation energies of the network and also the width of the defect energy levels [27]. A simple approach of using a single formation energy and discrete gap states has been applied by Müller et al [28]. It has been found that the equilibrium is dominated by states with the lowest formation energy and an approximation can be made where there is a small subset of network sites at which a defect can be formed. These sites are physically associated with weak bonds.

### 2.2.1 Distribution of formation energies (WB-model and role of band tails)

The formation of dangling bond defects is well described by the weak-bond-dangling bond conversion model (WB-model) originally proposed by Stutzmann [29]. According to this model, the Fermi energy moved into localized band-tail states would occupy antibonding levels of these states resulting into bond breaking and hence defect formation. Smith and Wagner [27] treated this process as a chemical reaction described as:

\[
\text{Weak bond} \rightleftharpoons \text{Dangling bond}
\]

With this consideration, Smith and Wagner calculated the density of neutral dangling bonds in undoped a-Si:H. They found that the distribution of formation energies according to the weak-bond-dangling bond conversion model has a shape proportional to the valence band tail density of states. Figure 2.2 shows the schematic density of states diagram illustrating the distribution of defect formation energies according to the weak bond to dangling bond conversion model. The distribution involves both an exponential component due to the exponential valence-band tail, and a gaussian component due to the distribution of virtual defect states. The distribution of virtual defect states is described by the distribution of energies at
which a defect could be created (the defect pool). Figure 2.2 depicts the conversion of weak bonds in the interval \( dE \) whose reaction enthalpy is the cost to remove a weak bonding state at \( E \) and create a defect state at \( E_0^D \). The mechanism of defect distribution in a-Si:H is thought to be mediated by hydrogen. This is because the breaking of one weak Si-Si bond creates two defects, but the equilibrium defect density is different if two defects are allowed to remain close together as a pair, compared to the situation when they are able to diffuse apart [6]. It is widely accepted that defect creation process can be mediated by hydrogen diffusion which allows the defects to occupy the Si-H sites from which hydrogen is removed. The evidence arises from the observations of hydrogen motion at the same temperature as the metastable effects. It has also been found that the activation energy of defect annealing is comparable with that of hydrogen diffusion [30]. The details of hydrogen participation and the models developed to explain the hydrogen mediated defect creation processes are beyond the scope of this thesis, we recommend interested readers to references [6,30,31,32].

The usefulness of the weak bond model is that the distribution of formation energies can be evaluated from the known valence band and defect density distributions. The WB-model provides a framework for understanding how the defect density varies with deposition conditions and the doping levels. It enables the calculation relating the defect density to measurable quantities.

**Figure 2.2:** The schematic diagram of the distribution of defect formation energies according to the weak-bond-dangling bond conversion model describing the metastable defect formation with a pool of defect states.
The nature of the dangling bond states

The dangling bond states in a-Si:H are amphoteric in nature, meaning that they can act as either donor or acceptor states depending on the Fermi level. The states of the dangling bond can occupy three different charge states: positively charged when unoccupied, neutral when singly occupied and negatively charged when doubly occupied. If a dangling bond is occupied by two electrons, the electron-electron interaction will raise the energy of the pair. The extra energy arising due to the interaction is known as correlation energy \( U \). For a given dangling bond, there are two transition energy; \( E^{+}/0 \) related to the +/0 transition and \( E^{0/-} \) related to the 0/- transition. The energy difference between these levels gives the correlation energy \( U \) which in this case is the energy required to add a second electron on a singly occupied dangling bond. A positive contribution to the correlation energy is obtained from the electron-electron interaction while the network relaxation will lower the energy of the electron pair and therefore gives a negative contribution to the correlation energy. The correlation energy is not accurately known, however from the low temperature dependence of spin density in a-Si:H, \( U \) is positive [33] and takes the values between 0.2-0.3 ev [34].

2.2.2 The defect pool model (Fermi-level dependence of defect formation energy)

Since the energy of a dangling bond state can take a range of values, the chemical equilibrium gives rise to an energy shift of the peak position of the defect states that are created in different charge states (0, -, +). This is what is called the defect-pool model [35]. The defect pool model was developed for the calculation and description of the density of dangling bond states distribution in a-Si:H. Though the origins of the defect pool model stem from the work of Bar-Yam and Joannopoulos [36], Powell and Dean [35] came up with an improved defect pool model which is widely used for the calculation of the defect states distribution and density in a-Si:H. The basic principle of the defect pool model is that defects are formed according to the weak bond breaking model described in the section 2.2.1 and illustrated in Figure 2.2. The model considers the involvement of hydrogen in the conversion process as described earlier. The defect pool model also considers that the equilibrium density of dangling bond states depends on the Fermi energy, which leads to a higher density of dangling bonds in doped a-Si:H than in undoped amorphous silicon. The equilibrium dangling bond density of states is computed by minimizing the free energy of the system of weak silicon bonds, dangling bonds and hydrogen bonds.

According to Powell and Dean’s [35] improved defect pool model, the density
Metastability of hydrogenated amorphous silicon

of states formed from weak-bond states at energy $E_t$ is given by:

$$D(E) = \int \frac{P(E)g_t(E_t)}{1 + \exp[2(\mu_d(E) - E_t)/kT]} dE_t$$  \hspace{1cm} (2.6)

where the weak-bond states identified with the valence band tail states are exponentially distributed according to the following formula:

$$g_t(E_t) = N_{v0} \exp \left[ \frac{(E_v - E_t)}{E_v0} \right]$$  \hspace{1cm} (2.7)

with $N_{v0}$ being the density of tail states extrapolated to the valence band mobility edge $E_v$ and $E_v0$ is the characteristic energy of the exponential band tail slope. Using the approximation that for $\mu_d < E_t$ all weak bonds states convert to dangling bond states, while for $\mu_d > E_t$ a Boltzmann fraction of states converts, Powell and Dean evaluated the integral 2.6 to obtain the density of states as:

$$D(E) = P(E)N_{v0} \frac{2E_v^2}{2E_v0 - kT} \exp \left[ -\frac{\mu_d(E)}{E_v0} \right]$$  \hspace{1cm} (2.8)

where $P(E)$ is the defect-pool function which describes the distribution of possible available sites for defect formation. The pool function is assumed to have a gaussian distribution given by the following formula:

$$P(E) = \frac{1}{\sigma \sqrt{2\pi}} \exp \left[ -\frac{(E - E_p)^2}{2\sigma^2} \right]$$  \hspace{1cm} (2.9)

where $\sigma$ is the width of the pool and $E_p$ is the energy of the peak of the defect pool. In the chemical potential $\mu_d$, which is the change of free energy in the system arising from the addition of one extra defect, we find a term that accounts for the energy of the defect which is dependent on its charge state and on the entropy related to the silicon-hydrogen bonding configuration. The chemical potential is given by the equation:

$$\mu_d(E) = E + kT \ln \left[ \frac{F_{eq}^0(E)}{2} \right] + \frac{ikT}{2} \ln \left[ \frac{iN_{db}^+/0(E)}{2HP(E)} \right]$$  \hspace{1cm} (2.10)

where $F_{eq}^0$ is the equilibrium occupation function for neutral defect states, $H$ is the hydrogen concentration and $i$ is the number of hydrogen atoms involved in the defect formation process.
By substituting the Expression 2.10 into Equation 2.8 and through appropriate rearrangements, Powell and Dean obtained the following expression for the defect density:

\[
D(E) = \gamma \left[ \frac{2}{E_v^0} \right] \rho^{kT/E_v^0} \left[ E + \frac{\rho \sigma^2}{E_v^0} \right] P(E/E_v^0) \tag{2.11}
\]

with

\[
\gamma = \left[ \frac{N_{v0} 2E_v^2}{(2E_v^0 - kT)} \right] \rho \left[ \frac{i}{2H} \right]^{-\rho^2} \exp \left[ -\rho \left( E_p - E_v - \frac{\rho \sigma^2}{2E_v^0} \right) \right] \tag{2.12}
\]

where

\[
\rho = 2E_v^0/(2E_v^0 + iK T) \tag{2.13}
\]

![Figure 2.3: The density of states distribution according to the defect pool model. The density of dangling bond states from the +/0 and 0/- electron transition energies are given as \( N_{db}(+/0) \) and \( N_{db}(0/-) \). \( N_{total} \) is the total density of states and \( N_V \) and \( N_C \) are the density of states of the valence and conduction bands respectively.](image_url)

Equation 2.11 is the principal expression for the equilibrium defect density and distribution which is maintained for temperatures above the equilibration temperature. Shown in Figure 2.3 is density of states (DOS) distribution in the mobility gap of the intrinsic a-Si:H at the centre of the p-i-n structure calculated with
the defect pool model of Powell and Deane [35]. The figure shows the density of dangling bond states from the $+/0$ and $0/-$ electron transition energies. The total density of states ($N_{\text{total}}$), the density of states of the valence band ($N_V$) and conduction band ($N_C$) are also shown. As will be seen in chapter 5, the Fermi-level dependence of the defect density of states has consequences for the spatial distribution of defect states in an amorphous silicon p-i-n structure.

2.2.3 Concluding remarks

The defect pool model has been successful in explaining the equilibrium defect density of states as a function of Fermi energy. In a detailed paper Schumm has attempted to use the defect pool model for describing the metastable defect structure [37]. Regardless of Schumm’s work and attempts by other workers [38], the defect pool model has not been successfully applied for describing the dangling bond distribution under non-equilibrium conditions. In this work, we will attempt to extend the defect pool model to non-equilibrium steady-state conditions such as light soaking. The major interest here is to investigate the contributions of the different charge states of the dangling bond to the Staebler-Wronski effect.