The review gives the introductory information on metastable light-induced degradation of amorphous silicon called the Staebler-Wronski effect (SWE). The paper highlights some recent developments in our understanding of the effect as well as some successes in reducing the SWE. The latest results of the author’s experiments on the metastable effects and the degradation in thin film transistors and solar cells are also presented.

Keywords: hydrogenated amorphous and microcrystalline silicon (a-Si:H), Staebler-Wronski effect (SWE), degradation of solar cells.

1. Introduction

In the last twenty years, extensive work has been carried out both to obtain a fundamental understanding of light-induced degradation and also to develop materials and devices that are resistant to this degradation process (see proceedings of MRS Spring Meetings, San Francisco USA, Symposium A, from 1997 to 2003).

The observation of metastable changes in a-Si:H goes back to the work of Staebler and Wronski, who found in 1977 that the dark conductivity and photoconductivity of glow-discharge deposited amorphous silicon can be reduced significantly by prolonged illumination with intense light. The observed changes were found to be reversible by annealing of the a-Si:H samples at elevated temperatures (≥150°C), and were attributed to a reversible increase in density of gap states acting as recombination centres for photoexcited carriers and leading to a shift of the dark Fermi level $E_F$ toward midgap [1]. Since this first report, light-induced metastable changes in the properties of hydrogenated amorphous silicon are referred to as the Staebler-Wronski effect (SWE).

The glassy or amorphous phase of a material may well be characterised by the fact that the configurational ground state is not given by an absolute and isolated minimum of the total potential energy, but rather by a more flexible arrangement of the atoms allowing configurations with different local minima of the potential energy separated by a more or less continuous distribution of potential barriers. The possibility of transitions between adjacent local potential minima in an amorphous solid leads to a number of processes [2]. Reversible photostructural changes and photodegradation are commonly observed in low coordination glasses and polymers but are unexpected in rigid four-fold coordinated structures. In crystalline Si, atomic motions that could produce coordination defects occur only near 1000°C. The low-anneal temperature of the light-induced defects in a-Si:H can be related to the diffusion of bonded hydrogen.

Historically, the most favoured model has been the hydrogen bond switching model [3] which proposes that photoexcited electrons and holes recombine at weak Si-Si bond locations, that the accompanying non-radiative energy release is sufficient to break the bond, and that a back-bonded H atom prevents restoration of the broken bond by a bond switching event. Another model known as the charge transfer model suggests that preexisting spineless centres (positively and negatively charged dangling bonds) are transformed to neutral dangling bonds by capture of excess carriers. Instead of “dangling bond” or “dangling bonds”, they are used db or dbs abbreviations in the paper, respectively.

The main material properties [2,4] that could play a role in the SWE are:

- disorder in the Si network,
- hydrogen concentration and its complex bonding structure,
- concentration of impurities.

From the experiments with extremely pure materials, with the oxygen concentration as low as $2 \times 10^{15}$ cm$^{-3}$, produced at the Electrotechnical Laboratory (ETL) in Tsukuba, Japan [5], it can be concluded that the light-induced effects are characteristic for the silicon-hydrogen network. Only at impurity concentrations higher that $1 \times 10^{18}$ cm$^{-3}$ a correlation can be found between the SWE and the impurity concentration.

Present theories of the SWE compile our consideration on the electronic and hydrogen energy states and on hydrogen diffusion [6]. About eleven years ago, an authoritative review [3] concluded that the SWE is understood, except for the range of H motion involved. Since that time, new
results have challenged these theories. These new findings include:
• lack of spatial correlation between the defects and hydrogen,
• observation that the SWE occurs at 4.2 K with essentially the same efficiency as at 300 K,
• realization that the effectiveness of light-induced defects as recombination centres depends on the light exposure conditions,
• discovery that not only defects are produced by extended light exposure but also larger structural changes in the material involving the Si network.

2. Creation and annealing of defects

Metastable defects can be created by: short pulses and extended light exposure, rapid quenching, charge accumulation, and double-injection currents [3,4], as well as by keV electron bombardment [7]. Shortly speaking, metastability requires an energy barrier between alternative states (e.g. A, B) and creation of defects by external excitation. The recovery process is achieved by the thermal excitation (Figs. 1 and 2).

\[ N_d(t) = \text{const } G^{2/3} t^{1/3}, \]

when \( N_d(t) \) is much higher than the equilibrium defect density. This relationship obviously explains the lack of reciprocity between intensity and time. Stutzmann and his co-workers explain this nonlinear dependence in the following way. Defects are created by nonradiative recombination of electron-hole pairs at spatially correlated tail states that correspond to the bonding and antibonding states of weak Si-Si bonds. The recombination releases about 1.5 eV energy that breaks a weak bond and generates a defect. To prevent the two neighbouring bonds from recombinating, a neighbouring hydrogen atom moves into separate the two dangling bonds. The defect pair may separate further by additional bond switching. In the annealing process, the hydrogen atoms revert back to their original positions. Hydrogen is thus directly involved both in the defect creation and annealing.

The model can explain the self-limiting nature of defect generation. Therefore kinetics can be fitted with a stretched exponential [8] that saturates at the defect density \( N_d \) between \( 5 \times 10^{16} \) cm\(^{-3} \) and \( 2 \times 10^{17} \) cm\(^{-3} \). At \( T > 80^\circ \text{C} \), saturation is affected by thermal annealing, and at the lower \( T \) by a light-induced recovery [9]. These competing anneal processes cause \( N_d \) to increase slightly with increasing \( G \) and decreasing \( T \). The efficiency of dangling bond creation is difficult to quantify because of the sublinear dependencies of Eq. (1). Roughly, \( 10^{24} \) cm\(^{-3} \) recombination events are needed to reach \( N_d = 10^{17} \) cm\(^{-3} \) in undoped a-Si:H. The degradation rate is about three times larger in n-type a-Si:H, and 10 times larger in p-type a-Si:H, doped with 100 ppm P or B dopants, respectively. This trend follows the increase in the H diffusion coefficient with doping [4,8].
3. Examples of the SWE in a-Si:H

Dark conductivity and photoconductivity of the PECVD deposited a-Si:H thin film is presented in Fig. 3. Kinetics of the defect creation and the defect recovery measured by the author [10–12] are shown in Fig. 4. Similar results were presented earlier by Street [13]. The author’s samples are 0.8 µm thick p-i-n diodes with the areas about $10^{-2}$ cm$^2$. The current induced kinetics (defect creation and recovery) is discussed in sections 4 and 5.

Figure 5 shows bias-induced changes in a-Si:H thin film transistor (TFT) presented in Ref. 11. Figure 6 presents the bias induced threshold-voltage shift of a-Si:H thin-film transistors and recovery to the initial values reflect kinetics of reversible changes in a-Si:H [9]. The threshold voltage shift depends on microcrystallinity of intrinsic a-Si:H film in TFTs [14].

Light-induced degradation and light-induced recovery of the fill factor (FF) of a p-i-n solar cell are shown in Fig. 7(a) [15]. Exposure to 1-sun illumination (~0.1 W/cm$^2$) degrades FF from 0.67 to 0.58. Under the same exposure, FF which was degraded by a previous 10-sun exposure, recov-

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![Contributed paper](image-url)
ers from 0.52 to 0.58, the 1-sun saturation value. Figure 7(b) shows that the corresponding degradation and light-induced recovery of the $\mu_t\tau_e$ product are partially correlated with those of FF [15]. A concentration of defects (not shown), in contrast, showed no such correlation.

Figure 8 shows that the rise of relative volume change ($\Delta V/V$) with the time of light exposure (0.3 W/cm$^2$) coincides with that of the light-induced defects [16]. A calculated $\Delta V/V$ per a new defect is about $3 \times 10^{-22}$, which is many times larger than a molecular Si unit in the lattice. This means either that each dangling bond involves a structural expansion over 20-times larger volume or that $\Delta V/V$ is not related to dangling bonds.

Changes involving bonded hydrogen in a-Si:H were detected [17]. The authors developed a sensitive differential method for detecting small changes of the 2000 cm$^{-1}$ stretching mode vibration of Si-H. One of their results is shown in Fig. 9. The white light intensity was 0.4 W/cm$^2$. The rate of change of $\Delta \alpha/\alpha$ follows a stretched exponential with the same dispersive parameter $\beta$ and time $\tau$ as that of the rise in the defect concentration $N/N$. That is a puzzling result because the number of defects $N = 10^{17}$ cm$^{-3}$ is much less than $N_H = 5 \times 10^{21}$ cm$^{-3}$ -- the number Si-H bonds.

It is important to show here a dependence of SWE on technology and moreover on a level of structural ordering of the amorphous films. A significant reduction in photodegradation of solar cells was achieved by using hydrogen dilution of silane-processing gas during film growth [9,10,18,19]. Beyond a certain dilution threshold value, the silicon films become microcrystalline. Just before this threshold is reached, one observes evidence of greater structural order or substantial regions of intermediate range order in the amorphous film. Transmission electron micrographs show the regions that have a crystalline-like appearance. The amorphous-microcrystalline phase boundary depends not only on the dilution ratio $R = [H_2]/[SiH_4]$ or $R = [H_2]/[Ar]$ but also on the film thickness $d$ as shown in Figs. 10 and 11 because the ordered regions grow with the growing film [12,19]. Other parameters affecting the evolutionary phase boundary are substrate material, deposition rate and temperature, and the frequency (13.6 or 80 MHz, or microwave) of the plasma-deposition process.

Analysing Figs. 10 and 11 we can work out two step optimisation process for a-Si:H p-i-n amorphous and microcrystalline solar cells leading to lower degradation of the tandem cells.
Let us consider the a-Si:H film preparation by the plasma-enhanced chemical vapour deposition at 13.6 MHz frequencies (RF-PECVD) from SiH\(_4\) diluted 10:1–20:1 with H\(_2\) at the substrate temperature between 200–300°C. The mean concentration of hydrogen is about 10% and depends little on the preparation conditions. NMR studies revealed that about 4 at.% H is in a dilute phase, atomically dispersed and bonded as monohydride (Si-H). About 1 at.% is found as H\(_2\) located interstitially and in voids [20]. The rest forms clusters of about 6–8 Si-H bonds, presumably at internal surfaces of di- or tri-vacancies [2].

4. Nature of a-Si:H and metastability

Let us consider the a-Si:H film preparation by the plasma-enhanced chemical vapour deposition at 13.6 MHz frequencies (RF-PECVD) from SiH\(_4\) diluted 10:1–20:1 with H\(_2\) at the substrate temperature between 200–300°C. The mean concentration of hydrogen is about 10% and depends little on the preparation conditions. NMR studies revealed that about 4 at.% H is in a dilute phase, atomically dispersed and bonded as monohydride (Si-H). About 1 at.% is found as H\(_2\) located interstitially and in voids [20]. The rest forms clusters of about 6–8 Si-H bonds, presumably at internal surfaces of di- or tri-vacancies [2].

4.1. Hydrogen-mediated weak bond/dangling bond conversion and distribution of localised defect states in a-Si:H

Characteristic feature of amphoteric defects is the (effective) electron correlation energy \(U\), required to place a second electron on a singly occupied, isolated defect level. If \(U\) was negative, the majority of defects in undoped a-Si:H would be negatively charged (requiring \(-|U|\) less energy for formation) and the number of neutral defects (and, therefore, spins) would depend on the Fermi-Dirac occupation function and, therefore, strongly on temperature. The fact that the number of spins in undoped a-Si:H measured by electron spin resonance (ESR) is independent of temperature below 300 K is a clear and unambiguous signature for defects with a large, positive correlation energy [2–4,21].

One of the first and simplest model of the distribution of defect states in a-Si:H was the energy level ordering scheme for a single, isolated defect with a positive correlation energy. Let us assume that singly occupied defect state has an energy \(E_{D^0}\) in the a-Si:H gap. If the electron is removed by adding shallow acceptors, for instance, the resulting \(D^+\) state will appear at the same energy \(E_{D^+} = E_{D^0}\). Adding a second electron to the isolated \(D^0\) state results in a defect energy shift to \(E_{D^2} = E_{D^0} + U\), as illustrated in Fig. 12(a). This defect energy ordering scheme, with added broadening to allow for the disorder (Fig. 13), served as the basis for interpreting a number of transport, luminescence, and other optical experiments for many years [4].

New spectroscopic techniques measure the energy distribution of defect states throughout the gap [2,6,22] and clearly show that the energy relationship between \(D^-\) defects in n-type a-Si:H and \(D^0\) defects in undoped a-Si:H is such that \(E_{D^-} - E_{D^0} = -0.1\) eV. The measured defect level energy ordering is shown in Fig. 12(b). It is clear from a
comparison of Figs. 12(a) and 12(b) that the measured defect levels in a-Si:H do not behave as expected for a single, isolated defect. A pairing between dopants and defects, which would reduce the Coulombic portion of the correlation energy, has been proposed to account for this behaviour [23]. However, this defect energy ordering has been observed in a variety of situations where either the dopant chemistry is substantially different from the usual substitutional dopants, or dopants are absent altogether.

An alternative explanation proposes a pool of defect sites from which the system can choose to create or destroy defects in order to minimise the system free energy [6,24].

4.2. Simple models describing electronic states in a-Si:H and energy distribution of hydrogen

Figure 14 is a sketch of the electronic density of states and, on the left-hand side, the assignment of these states to bonding \(VB\) = valence band), nonbonding \(D = neutral and D^- = charged dangling bonds), and antibonding states \(CB = conduction band\). The dashed lines at 0 and 1.8 eV indicate the mobility edges; i.e., the demarcation energies between the extended states and the localised states that tail from \(E_v\) and \(E_c\) into the gap. The \(29\)Si hyperfine structure of the electron-spin resonance (ESR) signal from electronic trapped in a deep \(CB\) tail state show the wave function spread over only two Si atoms, as one would expect for an electron in an antibonding state of a weak Si-Si bond [25]. In contrast, hopping transport in these tail states yields localisation radii between 0.5 and 1.0 nm, which suggests that the wave functions are not confined to a weak bond, but rather are spread over strained regions [2]. These two experiments may measure different parts of the wave function, the central region in one case and the exponential tail in the other. In the following we make the simplifying assumption that tail states are associated with one weak Si-Si bond, or antibond. The density of states at \(E_v\) and \(E_c\) is about \(10^{21} \text{eV}^{-1} \text{cm}^{-3}\); the exponential tail slopes are \(E_0 = 0.05 \text{eV}\) for the valence bond tail and 0.025 eV for the conduction bond tail. Hence, there are only about \(10^{19} \text{cm}^{-3}\), so-called, weak bonds, out of a total of \(10^{21} \text{cm}^{-3}\) bonds. According to the energy scale of Fig. 14, it costs \(2 \times 0.5 \text{eV}\) to break a weak bond. Therefore they form two \(D^+\) states because two \(VB\) tail electrons are lifted from the level 0.3 eV to 0.8 eV – the location of \(D^+\). Local relaxations and charge transfers to the \(D^+\) states lower this energy. The majority of bonds are stronger and the defect-formation energy higher.

Figure 15 shows the H density of states derived from these considerations. Two dangling bonds are created by lifting one H into Si-Hdb states, H becomes mobile when it is among the majority of states near \(E_t\) (the transport energy for H atom in a-SiH) and no longer restricted to the

\[
\begin{align*}
\text{Staebler-Wronski effect in amorphous silicon and its alloys}
\end{align*}
\]
~$10^{19}$ cm$^{-3}$ weak bond states, which are considerably lower than $E_i$ and, hence, not mobile without further activation.

### 4.3. H-bonding states in a-Si:H and hydrogen diffusion

The $10^{17}$ cm$^{-3}$ SWE defect must come from breaking Si-Si or Si-H bonds. However, $N = 10^{17}$ cm$^{-3}$ is a small fraction of $5 \times 10^{23}$ Si-H bonds and, say, $10^{23}$ cm$^{-3}$ Si-Si bonds. Moreover, it takes $10^7$ photons to produce one dangling bond.

Diffusion of H in a-Si:H probably occurs by thermal dissociations of H from an isolated Si-H or 2H from a (–U) pair state. Possible reactions are as follows:

<table>
<thead>
<tr>
<th>Possible reaction</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Si + Si-H $\rightarrow$ Si-db + Si-H-Si</td>
<td>defect + interstitial (dissociation), (2)</td>
</tr>
<tr>
<td>Si-Si + 2Si-H $\rightarrow$ 2Si-db + Si-H-Si</td>
<td>defects + (Si-H bonds + clustered H or H$_2^*$ molecules) (dissociation), (3)</td>
</tr>
<tr>
<td>Si-H-Si + Si-Si $\rightarrow$ Si-Si + Si-H-Si</td>
<td>mobile hydrogen, (Si-H-Si is also written as Si-Hdb). (4)</td>
</tr>
</tbody>
</table>

Near 300°C, hydrogen begins to effuse from a-Si:H without significantly changing the dangling bond defect concentration $N$ [10]. This means that the broken Si bonds left behind must be close pairs which reconstruct to a Si-Si bond, albeit weak and stretched. Taking one H atom from these pair sites leaves behind dangling bonding, which costs energy. Taking two H atoms costs less because a Si-Si bond is formed. This feature leads to the negative effective correlation energy ($–U$) of H pair states in clusters. Hydrogen can be reintroduced into a-Si:H from the H plasma, essentially without a change in $N$, which proves the presence of empty H pair states; i.e., presumably stretched Si-Si bonds. At the higher temperatures, near 500°C, H from the isolated Si-H bonds effuses, leaving behind dangling bonds. The density of states of the H bonds can be deduced from the hydrogen effusion experiments.

Diffusion of H in a-Si:H probably occurs by thermal dissociation of H from an isolated Si-H or 2H from a (–U) pair state into a Si-H-Si centred bond state. In a-Si:H, the H is somewhat off the centre line. If shifted closer to one Si, the Si-H-Si structure resembles a Si-Hdb pair. The Si-H-Si centre bond has been observed on repolarisation measurements. The Si-Hdb is mobile with an estimated $E_t$ = 0.3 eV saddle point energy by insertion of H into a neighbouring Si-Si and reforming the broken bond left behind.

Two points should be emphasized. The Si-H bonds have nearly the same energy because H is unconstrained. Evidence for this is the common Si-H stretching mode at 2000 cm$^{-1}$. The effect of the different energies of the three Si back bonds is relatively small. The largest energy for the dissociation [reactions (2) and (3)] arises from the creation of the two dangling bonds appearing on the right-hand side. Dangling bonds result in electronic midgap states which can capture either an electron or a hole from the Fermi energy $E_F$ thereby lowering the defect formation energy. Thus, the energy spectrum of hydrogen states depends on the spectrum of electronic states related to Si-Si and Si-H bonds, as well as on the $E_F$ and the presence of photo-excited carriers.

In equilibrium above $T_E$ (initial equilibrium temperature), a hydrogen chemical potential $\mu_H$ is established, and the hydrogen diffusion constant $D_H$ is activated by $E_D = (E_i - \mu_H) = 1.5$ eV. The calculations agree well with the experimental value. The (–U) H pair states mentioned above are very important but have not been included in Fig. 15. In a sense, these states are below and above $\mu_H$ and they pin $\mu_H$. However, the pair-states statistics require the use of the partition function instead of the Fermi function and should not be plotted a scale of one-H density states. The

\[
\text{Si-H states are about 0.3 eV below } \mu_H, \text{ as deduced from the temperature dependence of } N \text{ in equilibrium above } T_E.
\]

This is the observation of a time dependence of the diffusion coefficient

\[
D_H = D_0 \beta^{-1}.
\]

With $\beta = 0.8$, measured at 250°C in 1 at.% B-doped a-Si:H, which likely results from multiple trapping of the diffusing H in the distribution of H states below $E_i$ in Fig. 15, the distribution having the logarithmic width $kT_E$, which would yield $\beta = T/T_E$.

The H glass model yields the thermodynamics equilibrium concentration of dangling bond defects as a function of temperature and Fermi level position, as well as temperature dependence of the doping efficiency and the density of defects as a function of doping. The concentration of defects and dopants equilibrated at $T > T_E$ can be measured by lowering temperature when they are metastable. They relax by the annealing to their equilibrium concentrations. Hydrogen diffusions enter the calculations only for explaining the kinetics of the defect and dopant reactions. Even if our understanding of the microscopic steps of diffusion will change in the future, perhaps forcing us to replace Eqs. (2) to (4), the explanation of the kinetics will remain the same as it rests more on Eq. (5) and the measured diffusion activation energies.

As an example, Fig. 6 shows the kinetics of metastable defect creation by abruptly changing the gate voltage $V$ and, hence, the accumulated charge in a field effect transistor and the subsequent relaxation as $V$ is removed. The kinetics can be described by a stretched exponential

\[
N(t) = N_s - (N_s - N_0) \exp[-(t/\tau)\beta].
\]
Here, \( N(t) \) is to be understood as newly created metastable defects, according to the turn-on voltage of the FET. The subscripts \( s \) and \( o \) refer to saturation and initial, respectively. Defect and dopant creation and relaxation follow Eq. (6), where the value of \( \beta \) was found to be the same as in Eq. (5) of H diffusion. The activation energy of \( \tau \) is about 1 eV, which agrees with that for diffusion over a constant distance. This refinement is necessitated by the dispersive nature of diffusion (Eq. 5). This establishes link between creation and relaxation and H glass model and the involvement of H in the metastability reactions.

5. New experimental data and theories of metastability

It is noteworthy that Stutzmann’s model, described in the earlier paragraphs, assumes that the defect creation events have a very localised nature.

Currently, there are experimental results that do not support the local microscopic models while novel characterisation techniques are able to detect light-induced changes that affect regions of the Si network that are much more extended. Firstly, the pulsed ESR experiments [25] show that there is no close spatial correlation (within 0.8 nm) between light-induced dangling bonds and hydrogen as would be the case in the hydrogen bond switching model. A further problem with the H bond switching model is that dangling bonds can in practice be created with the same efficiency at 4.2 K as at 300 K and significant annealing of defects created at 4.2 K occurs at the temperatures well below 300 K [24], whereas hydrogen is basically immobile at these temperatures, even under intense illumination. The charge transfer model has also become increasingly unlikely, since the subgap absorption as measured by photothermal deflection spectroscopy (PDS), which is equally sensitive to transitions from charged or neutral states, correlates well with the ESR spin density for stable as well as for light-induced defects [3]. The strong correlation does not make it likely that there is a significant contribution of ESR-inactive charged dangling bonds to the SWE.

Increasing evidence suggests that the SWE is sensitive to the hydrogen microstructure and should be detectable as a collective change in the Si network. Hydrogen bonded in the configurations leading to the high microstructure parameter \( R^* \) (amorphous phase to single crystal phase ratio) was shown to give rise to the faster metastable defect creation kinetics [2,6]. Whereas hydrogen in the clustered phase affects the kinetics of the SWE, the saturated density of metastable defects is correlated with the hydrogen in the dilute phase (i.e., yielding stretching mode vibrations only at 2000 cm\(^{-1}\)). The light-induced defects could be found in H-poor regions only, not in hydrogen rich regions.

Accumulating evidence is available now that the SWE manifests itself in the changes that are extended over large regions of the silicon network, but perhaps still limited to those regions where hydrogen is dispersed and purely bound as monohydrides up to the solution limit of 2–4% [26,27]. The following observations cannot be explained by the localised bond-switching and charge-transfer events alone:

- \( \mu\tau \)-product is not a single-valued function of the dangling bond concentration as measured by optical techniques [6,24],
- change in the proton nuclear magnetic resonance (NMR) dipolar spin relaxation time upon light soaking was found to involve 10% of the 3×10\(^{21}\) cm\(^{-3}\) bonded hydrogen atoms [22]. This can only be understood if the structure of the Si network changes in an extended volume since only then the dipolar spin lattice relaxation times of many hydrogen nuclei can be affected,
- Si 2p peak detected by core-electron X-ray photoemission spectroscopy (XPS) was found to shift reversibly upon light soaking to a lower binding energy, which implies that not only the Si atoms nearest to the 10\(^{17}\) cm\(^{-3}\) metastable defects are affected, but also those in an extended region outside of the nearest neighbour shell [28],
- distinct change in the 1/f noise statistics upon light soaking from non-Gaussian to Gaussian suggests collective long-range interactions rather than locally isolated bond-breaking [8],
- ratio of anisotropic to isotropic polarised electroluminescence appears to undergo significant changes before the metastable defects appear in CPM measurements on the same sample [29]. This ratio reflects the bond angle disorder in the silicon network and indicates that dangling bond creation is proceeded by long range network strain,
- infrared spectroscopy measurements revealed a reversible significant increase in the monohydride absorption mode after light soaking [17]. A possible explanation is that the oscillator strength of this mode has increased due to a structural change of the silicon matrix,
- recently it was shown that even the geometrical volume of the material may change due to light soaking [16]. The photodilatation effect takes place instantaneously when the sample is exposed to light. Although the photostructural origin of the transient effect has been called in question, the remaining dilatation after extended light exposure [29] and the change in the law frequency dielectric constant after the exposure [30] are observations that once more suggest that macroscopic changes take place in the Si network.

The observations of large scale structural changes listed above support the viewpoint that long-range motion of configurational defects is taking place during light soaking [28]. These transporting configurational defects can be mobile dangling bonds, floating bonds, excited hydro- 

drogen in transport states, or complexes of one or more
dangling bonds and hydrogen at a transporting energy level [21]. The hydrogen collision model is consistent with the spatial separation of light-induced dangling bonds and hydrogen, the observed kinetics under continuous and pulsed light soaking, and the observed macroscopic structural changes, however, the ultimate proof would come from the detection of \( \sim 10^{17} \) cm\(^{-3} \) metastable complexes of two Si-H bonds.

Branz model [21] suggests that the dissociation Eq. (2) occurs during a recombination process at a rate proportional to the recombination or the \( e-h \) generation rate \( G \), as in a geminate recombination process. The mobile Si-Hdb, which is also considered to be the mobile species in H diffusion theories, moves through the material. When it meets a dangling bond, it is annihilated via the reverse Eq. (2). Hence, its lifetime is proportional to \( 1/N \). Occasionally, one Si-Hdb meets another Si-Hdb. This is called an H collision, which results in a metastable Si-HH-Si state. The writing HH between two Si does not reflect the true structure of this metastable state. Because the probability of two unrelated Si-Hdbs colliding, each having a lifetime \( \sim 1/N \), is proportional to \( G^2/N^2 \), which yields the desired kinetics of Eq. (1). Thermal- and light-induced annealing occurs by breaking up the metastable Si-HH-Si state into two mobile Si-Hdb species. These, in turn, meet dangling bonds by diffusion and annihilate. The observed metastable dangling bonds are spatially isolated from H as well as from each other because the concentration of mobile Si-Hdbs always remains small compared with \( N \). It is important to make a distinction between the metastable state Si-HH-Si and the large concentration of \( (-U) \) pair states mentioned above in order to explain that both light-induced annealing as well as thermal annealing have \( E_A \) smaller than the activation energy of diffusion. If the two were identical and easily dissociated by a recombination process, one would be able to remove all \( N \) by light-induced annealing, and there would be no SWE [21].

Recent research targeting at “more stable” materials seems to be successful by addressing the role of hydrogen (e.g., by depositing device-quality material with a very low hydrogen content [15]) or the role of the microstructure (e.g., by depositing nanostructured silicon from a plasma close to the powder regime [31]). The latter material comprises crystalline-like regions where no defect creation takes place, probably because configurational defect motion does not take place in these regions, whereas the surrounding material contains more clustered hydrogen in which no large-scale photostructural strain builds up. Previously, these two phases have also been observed in deuterated materials which appeared to be very stable [18]. The existence of these two phases might also be the origin for the observed near-perfect stability of a-Si:H TFTs made by hot wire deposition [18]. Another approach is to avoid amorphous regions altogether and introduce polycrystalline thin films (with either nanometer-scale grains or larger) as the photoabsorber film in photovoltaic devices.

The question of a spatial correlation between H and dangling bonds is an important issue but is not used to disqualify any theory as previously stated in this review. Building on the success in explaining defect and dopant equilibration, the equilibrium models mentioned in the section on hydrogen in a-Si:H have been extended to explain the SWE. An important ingredient of these theories is the close link between electronic and hydrogen energy states and the dependence of the defect formation energy by transferring electrons between the Fermi energy and the defect states. The logical extension of these models holds that illumination increases the dangling bond concentration because the excess electrons and holes described by the splitting of \( E_F \) into quasi-Fermi levels reduce the energy barriers for defect formation and the defect formation energies. With plausible assumptions, these theories produce kinetics similar to Eqs. (1) and (6), and agreements with the observed magnitude and temperature dependence of the saturation value \( N_s \) above 250 K.

Godet [23] has suggested a metastable H trapping model (MSH): A \((-U)\) pair states exists, designated Si-HH-Si. An \( e-h \) pair recombination event initiates dissociation according to Eq. (3). When the mobile Si-Hdb species produced thereby meet a dangling bond, they annihilate. If either one meets an isolated Si-H, on the other hand, an isolated dangling bond is produced as well as a new \((-U)\) pair state according to reaction

\[
\text{sSi-Hdb} + \text{Si-H} \rightarrow \text{db} + \text{Si-HH-Si}. \tag{7}
\]

The models discussed so far involve H motion and yield defects in close spatial proximity with H, the Si-Hdb state of Eq. (2) or, alternatively, the dangling bond close to Si-HH-Si in Eq. (7).

We now compare these models with the experimental results. The equilibrium models, as well as Godet’s MSH model and Branz’ H collision model, require diffusion of mobile Si-Hdb species; the first require diffusion over a distance of about 1 nm, the average separation of Si-H and Si-HH-Si, whereas the H collision model deals with diffusion distances of 20–50 nm, the average separation of metastable dangling bonds. We should note that the diffusing Si-Hdb species have already been created by a recombination process and only have to overcome the barriers associated with Eq. (4).

One major difference between the H collision model, on the one hand, and the bond-breaking model, on the other, is the nature of metastability. In the latter, the metastable state is the Si-Hdb whose energy distribution forms the tail of energies below the transport energy \( E_T \) in Fig. 15. The large anneal energy \( E_A = -1 \) eV of dangling bonds created at \( T = 300 \) K indicates that the mobile Si-Hdb species have found some deep traps; i.e., the low-lying Si-Hdb states associated with weak bonds. Many dangling bonds created at low \( T \) have the much smaller \( E_A \), as shown in Fig. 7. These Si-Hdb species appear to occupy


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the shallow traps or H energy states not far below the transport energy $E_i$ in Fig. 15. They have not moved far from their dangling bond partner and hence, do not have a chance to get more deeply trapped in a weak bond state. In the H collision model, in contrast, the metastable state is Si-HH-Si*, whereas the Si-Hdb species are very mobile and able to diffuse over 20–50 nm distances. This high mobility is the largest conceptual difficulty of this model. Light-induced H diffusion is known to exist, and a recent experiment succeeded in measuring $D_H$ at 135°C under illumination with $G_D = 10^{23}$ cm$^{-3}$s$^{-1}$. At this temperature, $D_H$ with light is still thermally activated with 0.9 ±0.1 eV. A temperature-independent regime of the light-induced $D_H$ has not yet been found that would explain light-induced H emission and diffusion at low temperatures. This problem has been discussed by Branz [21] who concludes that the question is still open. It seems that an attempt to measure $D_H$ by using very long exposures to strong light at 300 K or below might find a value for $D_H$ that is either too small or acceptable for the H collision model to work. Evidence for long-range H diffusion under 15 W/cm$^2$ illumination at 300 K from a-Si:H into an a-WO$_3$ overlayer has recently been discovered. Fedders has provided calculation for a variety of pathways for H diffusion in a-Si:H and they all depend on the doping of the samples. This is qualitative agreement with Branz measurements. All calculations reported were obtained with ab-infinito, fully self-consistent, local orbital molecular dynamics (MD) code Spanish initiative for electronic simulations with thousands of atoms called SIESTA. The results are shown in Fig. 15 [32].

Every year brings new data. One of the last was high-resolution magnetic resonance (HNMR) experiment. Su $et$ $al.$ [22] have discovered a new type of hydrogen site in a-Si:H that appears after light-soaking. These sites consist of paired hydrogen atoms that are separated by about 2.3 ±0.2 Å. The density of these sites is between $10^{17}$ and $10^{18}$ cm$^{-3}$. The behaviour of these sites upon annealing is similar to that of the defects produced during light soaking. This evidence strongly suggests that these sites are correlated to the metastable defect production during light soaking [22].

6. Methods of reducing the SWE

The metastable dangling bonds have an energetic and spatial distribution which determines their charge state. The space charge distribution of the charged states then modifies the internal electric field profile, which in turn has an additional effect on the carrier collection in the device.

Furthermore, the optimal electric field profile limits possibility of band-to-band electron-hole recombination and therefore it is effective method of the SWE reducing. During the measurements the following are taken to attention: the largest relative changes occur in the fill factor, the relative changes in the short circuit current are significantly smaller, whereas the open circuit voltage usually does not degrade.

Single junction cells:
- with a thick intrinsic layer degrade deeper than those with a thin intrinsic layer;
- with a high impurity concentration (above $10^{18}$ cm$^{-3}$) in the intrinsic layer degrade deeper than those with high purity intrinsic layers;
- operated at elevated temperatures (60–90°C) stabilise at the higher efficiency than those operated at a room temperature or below;
- cyclic exposure results in stabilisation at the higher efficiency than a continuous exposure;
- exposure to high intensity illumination causes deeper degradation than to 1-sun illumination; illumination levels less than 100 mW/cm$^2$ lead to reduced degradation.

An engineering solution is to make the intrinsic absorber material as thin as possible in order to maintain a high electric field after degradation. At the same time, the absorbed fraction of the incident light is maximised by utilising optical light confinement techniques made possible by the textured electrodes and enhanced multilayer back reflectors. Next, using microcrystalline Si and Ge films additionally, reducing of the SWE is possible. It can be seen in Figs. 16 and 17.

Recent experiments [33] with hydrogenated Si-Ge alloys show an unexpected interrelation between Si dangling bonds and Ge dangling bonds. The total dangling bond concentration (but not the individual ones) is proportional to $t^{0.5}$ during exposure.

7. Conclusions

A newly modified model for metastability has been proposed recently by Branz [21] that postulates formation of a metastable complex containing two Si-H bonds. Light exposure generates the electron hole pairs that recombine through multiphonon excitation of Si-H vibrations. The recombination breaks the Si-H bonds and promotes H to a
transport state. Molecular dynamics calculations show that a diffusing H-atom successively breaks Si-Si bonds creating Si bonds and a neighbouring dangling bond. When this mobile hydrogen in the form of Si-H and dangling bond pair meets another pair of the same kind, the two dangling bonds annihilate each other leaving behind a metastable complex of two Si-H bonds. Biswas and Pan showed \[34\] that formation of such a defect complex is indeed feasible, and they are the lowest energy configurations other than the initial state. Branz has been successful in explaining the kinetics of many of the defect creation and annealing behaviours using this model. To explain the kinetics of defect creation at low temperature, enhanced hydrogen diffusion due to carrier capture effects was postulated. Further studies will be necessary to explain the annealing behaviour in the dark at low temperatures when, usually, H diffusion will be negligible.

Light-induced degradation appears to be caused largely by one recombination process among several others. We have not clearly identified which one is the most harmful. The reduction of the SWE in high-electric fields suggests that geminate recombinations (i.e., recombinations of photoexcited electrons and holes associated with each other by one photon absorption event) play a role, whereas the rate equation \(dn/dt = -G^2N^2\) is based on bimolecular recombination of non-geminate carriers. Geminate processes are certainly excluded in current-induced defect creation in p-i-n junctions.

An excess concentration of electrons only (or holes) produces defects (shown earlier) as well as the charge injection in p-i-n junctions. The distinction between these mechanisms and the SWE is not clear.

The general trend of improving the stability of a-Si:H suggests that it is most important to decrease the presence of weak bonds. These give rise to deep traps for mobile hydrogen species in the density of H states. Without these deep traps, the anneal energy of the metastable SWE would be reduced as well as the magnitude of the SWE at (and above) room temperature.

Fig. 17. The normalized conversion efficiency for singles and triple junction solar cells as a function of time, exposed to suns illumination. There are shown differences of theirs stability (after Ref. 9).

References


