Research Article

Annealing Kinetic Model Using Fast and Slow Metastable Defects for Hydrogenated-Amorphous-Silicon-Based Solar Cells

Seung Yeop Myong
Department of Physical Electronics, Tokyo Institute of Technology (TIT), 2-12-1 Ookayama, Meguro-Ku, Tokyo 152-8552, Japan

Received 1 February 2007; Accepted 17 April 2007

Recommended by Armin G. Aberle

The two-component kinetic model employing “fast” and “slow” metastable defects for the annealing behaviors in pin-type hydrogenated-amorphous-silicon- (a-Si:H-) based solar cells is simulated using a normalized fill factor. Reported annealing data on pin-type a-Si:H-based solar cells are revisited and fitted using the model to confirm its validity. It is verified that the two-component model is suitable for fitting the various experimental phenomena. In addition, the activation energy for annealing of the solar cells depends on the definition of the recovery time. From the thermally activated and high electric field annealing behaviors, the plausible microscopic mechanism on the defect removal process is discussed.

Copyright © 2007 Seung Yeop Myong. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

1. INTRODUCTION

In recent years, there has been an explosive, worldwide increase in solar module market due to the global warming and oil crisis. Because bulk crystalline silicon (c-Si) modules make up 90% of products, a severe shortage of c-Si wafers has caused an increase in the cost of the bulk c-Si solar modules. Thus, the increased cost of c-Si wafers currently threatens the photovoltaic business. Thin-film Si solar modules using hydrogenated-amorphous-silicon- (a-Si:H-) based absorbers, meanwhile, become a promising alternative to the bulk c-Si solar modules, because of their remarkably low consumption of raw Si material (<1% of consumption of bulk c-Si modules), large-scale deposition, and low-temperature production. Furthermore, thin-film Si photovoltaic technology profits from the wide experience base of the display industries [1].

However, the so-called “Staebler-Wronski effect (SWE)” in a-Si:H-based films remains as a major obstacle to the commercialization of thin-film Si solar modules. SWE is the light-induced degradation arising from the photocreation of dangling bonds (DBs) accomplished by the nonradiative recombination of photogenerated electron-hole pairs [2, 3]. Because it severely limits the conversion efficiency of a-Si:H-based films, many researchers have investigated SWE during the past 30 years. Despite extensive investigations, there is no consensus on a microscopic mechanism that explains all the experimental phenomena. Similarly, the recovery mechanism for a-Si:H-based solar cells via thermal annealing [4, 5] or intense illumination at high temperature with a strong reverse bias [6] is still controversial. The recovery kinetics via thermal annealing is often interpreted by the stretched exponential (SE) kinetics [7, 8] wherein defect generation and annealing in a-Si:H-based materials is a dispersive process controlled by one type of metastable defect [9, 10]. However, several recent reports have provided experimental evidence that a-Si:H-based materials possess “fast” and “slow” metastable defects, and thus the total defect density cannot uniquely determine the state for the a-Si:H-based solar cells [11–14]. Yang and Chen suggested the existence of the fast and slow metastable defects in a-Si:H solar cells via two-step light soaking [11]; the cell subjected to an intense pre-soaking exhibits a thermal annealing behavior at the initial stage of 1-sun (AM 1.5, 100 mW/cm²) post-soaking, which could be linked to annealing of the fast metastable defects. Since these results are clearly contradictory to the conventional SE kinetic model, the author suggested a new model of recovery kinetics for pin-type a-Si:H-based solar cells employing the two-component (TC) metastable defect states [15]. We selected the fill factor (FF) as a measure of the state.
for the a-Si:H-based solar cells due to the following reasons: (i) FF is sensitive to the quality of the intrinsic absorber (i-absorber); (ii) analytic equations relating FF to the collection length and to the defect density (or electron spin density) have been developed [16, 17]; and (iii) FF is the most degraded parameter against light-soaking in a-Si:H-based solar cells [18] and is less sensitive to the measurement temperature and illumination intensity compared to the open-circuit voltage and short-circuit current [4].

In this work, the TC model is simulated by varying its parameters. The model is also applied to experimental annealing data for the pin-type a-Si:H-based solar cells in order to verify the validity of the TC model. Finally, the microscopic mechanisms for the annealing behaviors of pin-type a-Si:H-based solar cells are discussed.

2. **MODELING AND SIMULATION**

If uniform time of photogenerated carriers, there is otherwise no direct communication between the two defect components under fixed annealing conditions. Thus, the system of rate equations for both components can be described as [11]

\[
\frac{dN_F}{dt} = G_F(N_T - N_F - N_S) - A_F N_F, \\
\frac{dN_S}{dt} = G_S(N_T - N_F - N_S) - A_S N_S,
\]

where \( N_T \) is the total number of states which can be converted into defects, \( G_F \) and \( G_S \) are the respective constant defect generation coefficients for the fast and slow metastable defects, and \( A_F \) and \( A_S \) are the respective constant defect annealing coefficients for the fast and slow metastable defects. In the case of thermal annealing, we assume that \( G_F = G_S = 0 \) and \( A_F \gg A_S \). Then, the rate equations for \( N_F \) and \( N_S \) can be expressed as the following simple first-order approximations:

\[
\frac{dN_F}{dt} = A_F N_F = -\frac{N_F}{\tau_F}, \\
\frac{dN_S}{dt} = A_S N_S = -\frac{N_S}{\tau_S},
\]

where \( \tau_F \) and \( \tau_S \) are time constants for the fast and slow metastable defects. Accordingly, \( N_F \) and \( N_S \) can be given by

\[
N_F = N_{AS} \exp \left( -\frac{t}{\tau_F} \right), \\
N_S = N_{AS} \exp \left( -\frac{t}{\tau_S} \right).
\]

After replacement of \( N \) and \( d \) by (7), (4) becomes the following kinetic equation:

\[
\frac{\partial n}{\partial t} = \ln \left[ 1 + \alpha \exp \left( -t/\tau_F \right) + \beta \exp \left( -t/\tau_S \right) \right],
\]

where \( \alpha = N_{AS}/N_0 \) and \( \beta = N_{AS}/N_0 = 1/n - 1 - \alpha \) is the ratio of the photocreated fast metastable defect density to the initial defect density, and \( \beta(= N_{AS}/N_0) = 1/n - 1 - \alpha \) is the photocreated slow metastable defect density to the initial defect density. Therefore, annealing behaviors can be simulated by fitting three independent parameters, \( \alpha, \tau_F, \) and \( \tau_S \).

Figure 1 provides the simulated results as a function of time \( t \) using (8). As shown in the figure, four different recovery rates are inspected with \( t \): (i) initial fast rise when \( t < \tau_F \), (ii) moderate increase when \( \tau_S < t < \tau_{FS} \), (iii) fast increase when \( t > \tau_{FS} \), and (iv) slow increase in the last tail. Figure 1(a) shows that the increase in \( \tau \) increases with an increase in \( n \). The rate of the increase decreases with the increase in \( n \) when \( t < \tau_{FS} \). An increase in the fraction of the fast metastable defect \( \alpha/(\alpha + \beta) \) leads to a fast recovery, as shown in Figure 1(b). It is also found that \( \tau_F \) is mainly responsible for the initial rise, whereas \( \tau_S \) affects the last tail as well as the region when \( t > \tau_S \) (see Figures 1(c) and 1(d)).
3. RESULTS AND DISCUSSION

Figure 2 depicts the simulated results using the TC kinetic model for the experimental results with various thermal annealing temperatures ($T_A$) reported in [4]. The pin-type a-Si:H solar cell was fabricated via a dc glow discharge technique with a structure of glass/transparent conducting oxide (TCO)/hydrogenated p-type amorphous silicon-carbide (p-a-SiC:H)/undiluted i-a-Si:H ($\sim$520 nm)/n-type a-Si:H (n-a-Si:H)/Ti/Ag. FF$_i$ and the initial efficiency are 0.70 and 9%, respectively. In all measurements, the cell was degraded under the 1-sun illumination at 40°C for 64 hours. Thus, FF$_d$ is always fixed at 0.55 ($n = 0.32$). With an increase in $T_A$, $\tau$ declines remarkably.

Figure 3 displays information on evaluated $\tau$ for the simulated data in Figure 2. Here, $\tau_i$ denotes the time for FF to recover $i\%$ of its total degradation, that is, FF$_i$ − FF$_d$. As can be seen in Figure 3(a), $\tau_i$ is thermally activated, that is, $\tau_i = \nu_0^{-1} \exp(E_a/kT)$, where $\nu_0$ is the attempt frequency, $E_a$ is the activation energy, $k$ is Boltzmann’s constant, and $T$ is the absolute temperature. In [4], Bennett et al. demonstrated that the annealing behavior for their pin-type a-Si:H solar cells could be characterized a unique $E_a$ of 1.2 eV. They selected $\tau_{50}$ as a measure of $\tau_i$. From Figure 3(b), however, it
should be noted that \( E_d \) for pin-type a-Si:H-based solar cells depends on \( \tau_i \) and the TC model presents a gradual decrease in \( E_d \) and \( v_n \) with an increase in \( i \). These phenomena are mainly caused by the existence of the fast and slow metastable defects in the TC model.

Figure 4 compares the simulated results using the TC model for the experimental results reported in [6]. The pin-type solar cell was fabricated at \( \sim 200^\circ \text{C} \) via a plasma-enhanced chemical vapor deposition (PECVD) technique [5] with a structure of glass/SnO\(_2\)/p-a-SiC:H/H\(_2\)-diluted i-a-Si:H (\( \sim 300 \text{ nm} \))/n-a-Si:H/ZnO/Al. At the open-circuit, the cell was degraded under the 50-sun illumination at 60\(^\circ\)C for 30 minutes. Hence, \( n \) is always fixed at 0.43 by keeping \( F_f \) and \( F_F \) at 0.67 and 0.56, respectively. Then, the experimental recovery behaviors were inspected under 50-sun illumination with different \( V_a \). It was found that FF for the pin-type H\(_2\)-diluted a-Si:H solar cell recovered more rapidly under intense irradiation at \( T_A = 70^\circ\)C with an increase in reversed \( V_a \), \( \tau_F \) and \( \tau_S \) for the TC model all gradually decrease with the increase in reversed \( V_a \), thus indicating the high electric field induced fast recovery. The reduced \( \tau \) is mainly due to the decrease in \( \tau_S \). It is clear that the TC model fits the experimental data well in the initial rise and last tail. Furthermore, the reported different recovery kinetics from identical \( F_F \) and \( F_S \) during the light-induced degradation, prove that the photorecombination of DBs, that is, \( N_d - N_0 \), is composed of different kinds of defects.

The author has developed hydrogenated protocrystalline Si (pc-Si:H) multilayer absorbers [18]. The pc-Si:H material is a highly H\(_2\)-diluted a-Si:H material existing just below the threshold of the a-Si:H-to-\( \mu \)c-Si:H transition. Using a photoassisted chemical vapor deposition (photo-CVD) technique, we prepared alternately H\(_2\)-diluted i-pc-Si:H multilayers by modulating the mass flow control of the hydrogen dilution ratio (H\(_2\)/SiH\(_4\)), and thereby i-pc-Si:H has the repeatedly layered structure of low H\(_2\)-diluted a-Si:H sublayers and highly H\(_2\)-diluted sublayers. The highly H\(_2\)-diluted sublayers possess isolated nanosized Si (nc-Si) grains embedded in a-Si:H matrix [19]. The i-pc-Si:H multilayers exhibit a fast light-induced metastability with a low degradation. Consequently, highly stabilized solar cells (stabilized efficiency = 9.0\%) were achieved without using any back reflector [20, 21]. The pc-Si:H multilayer solar cells exhibit a very fast annealing behavior during 1-sun post-soaking, compared to a-Si:H solar cells [22], which is the clear evidence of the two-component metastable defects in the pc-Si:H multilayers. Figure 5 shows the fitted results using the TC model for the experimental recovery behaviors in an undiluted a-Si:H solar cell and a pc-Si:H multilayer solar cell in [8]. The pin-type solar cells were fabricated at 250\(^\circ\)C via a photoassisted chemical vapor deposition (photo-CVD) technique with a structure of glass/SnO\(_2\)/p-a-SiC:H/p-\( \mu \)c-Si:H/i-absorber (\( \sim 550 \text{ nm} \))/n-\( \mu \)c-Si:H/Al. The initial efficiency for the undiluted a-Si:H and pc-Si:H multilayer solar cells are 10.6 and 8.9\%, and FF values are 0.73 and 0.69, respectively. The solar cells were degraded under the 1-sun illumination at 48\(^\circ\)C for 20 hours. After light soaking, the pc-Si:H multilayer cell stabilized with \( n = 0.57 \), while the undiluted a-Si:H cell is still in degrading state with \( n = 0.39 \). The fitting parameters of the cells are listed in Table 1. Thermal annealing is performed in a vacuum chamber. The pc-Si:H multilayer cell exhibits the rapid recovery than the undiluted a-Si:H cell.

Table 1: Fitting parameters used in Figure 5.

<table>
<thead>
<tr>
<th></th>
<th>( n )</th>
<th>( \alpha/(\alpha + \beta) )</th>
<th>( \tau_F ) (min)</th>
<th>( \tau_S ) (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>undiluted a-Si:H</td>
<td>0.39</td>
<td>0.82</td>
<td>3.7</td>
<td>214.6</td>
</tr>
<tr>
<td>pc-Si:H multilayer</td>
<td>0.57</td>
<td>0.84</td>
<td>3.3</td>
<td>59.5</td>
</tr>
</tbody>
</table>


From the fast metastability and annealing behaviors of pc-Si:H multilayer solar cells, the vertically regular distribution of the isolated nc-Si grains [21] and the improved medium-range order in the a-Si:H matrix [23] are considered to localize the photorecreation near the grain boundary regions [19], and thereby suppress the photorecreation of slow metastable defects in the pc-Si:H multilayers. From the visible photoluminescence (PL) peak measured at room temperature, the isolated nc-Si grains tend to act as radiative recombination centers of captured carriers, which may contribute to the good stability [14].

Because the pc-Si:H multilayer has a slightly wider optical band gap (effective band gap \( > 1.7 \text{ eV} \)) than conventional a-Si:H layers (\( \sim 1.7 \text{ eV} \)), the pc-Si:H multilayer solar cell is promising as a top cell for a high-efficiency tandem cell [23]. The pc-Si:H multilayer/\( \mu \)c-Si:H (\( \sim 1.1 \text{ eV} \)) double-junction tandem structure opened the possibility of a significantly
high-stabilized efficiency due to a low-degradation ratio [24].

The photocreation of DBs in an a-Si:H matrix can occur with a value of $E_a$ [25] that is lower than $E_a$ for light-induced long range H diffusion (0.9 eV) [26]. Hence, the breaking of strong Si–H bonds (∼3 eV), proposed by Branz in the hydrogen collision model [27], cannot be easily accomplished by the nonradiative recombination of electron-hole pairs. Instead, the breaking of weak Si–Si bonds due to nonradiative recombination of electron-hole pairs is considered today as a plausible origin of SWE [28, 29]. Recently, Powell et al. [29] proposed the creation of two metastable HSiDB (complex of...
a DB and an Si–H bond, where H locates in a tetrahedral-like site (Td site, not a bond-centered site) defects; an H atom from a neighboring doubly hydrogenated weak Si–Si bond (HSiSiH) switches to a Td site of the broken Si–Si bond and the other H from HSiSiH is also located in the energetically suitable Td site. This model is reasonable because the spatial separation between H in the Td site and DB is in agreement with the observed values of 4–5 Å by electron spin resonance (ESR) measurements [30]. On the other hand, it has been reported that annealing of DBs in a-Si:H films, which are photocreated at moderate temperature, has a similar value of $E_a$ (1.1–1.2 eV) [31] to that for long range H diffusion (1.5 eV) [32]. This supports the supposition that long range H diffusion plays an important role in annealing of metastable defects. Thus, the hydrogen collision model is valid in the case of annealing and $E_a$ can be interpreted as the energy for the thermal emission of H from a Td site. In addition, $\nu_\alpha$ corresponds with the phonon frequency of Si–H bonds [29] and with the thermal emission process. However, it is difficult to define unique $E_a$ and $\nu_\alpha$ for $\tau$, because it varies with $\tau$ (see Figure 3(b)). Nevertheless, $E$ in a solar cell is expected to lower the energy barrier for long range H diffusion [6]. From Figure 4, it can be concluded that the intense illumination at a high temperature also thermally emits mobile H by breaking Si–H bonds, and leads to high electric field induced annealing for the solar cells.

In the previous report [15], the author proposed the following mechanism for the recovery kinetics in pin-type a-Si:H-based solar cells based on the TC model: (i) mobile H is thermally emitted from a metastable HSiDB defect by breaking the Si–H bond. As reflected in Figure 2, the elevated $T_A$ increases the thermal emission rate of mobile H [32]; (ii) emission of bonded H is followed by weak Si–Si bond reconstruction. Meanwhile, mobile H migrates through the lattice [33, 34] and is subsequently captured at another weak Si–Si bond, which eventually forms an HSiDB defect. It should be noted that $E$ in i-absorber assists the migration of mobile H to a shallower site, which is reflected in Figure 4; and (iii) thermal emission and recapturing processes of mobile H proceed until it is captured at the DB site of a metastable HSiDB defect, resulting in the annealing of two defects. Consequently, for the annealing process to reform the a-Si:H matrix, a considerable energy is required and many H atoms are involved. However, an internal field formed in solar cells can reduce the required energy for the annealing process. It should be noted that the classification between the fast and slow metastable defects is mainly determined by their activation energy and capture cross-section [14]. This classification is only relative and is dependent on the annealing conditions, that is, elevated $T_A$ or $V_a$ can increase $\alpha$.

4. CONCLUSIONS

The author simulated the TC model in order to understand the effect of each parameter on the annealing kinetics in pin-type a-Si:H-based solar cells. This model displays that $E_a$ depends on the definition of the recovery time. It is verified that the TC model fits the various experimental data. Thus, the TC model can be deemed useful for limiting the number of mechanisms responsible for annealing the photocreated defects in a-Si:H. From the thermally activated and high electric field induced nature of annealing behaviors, the plausible microscopic mechanism on the DB defect removal related to the
thermal emission of mobile H from $T_d$ sites and long range H diffusion was discussed.

REFERENCES


Submit your manuscripts at http://www.hindawi.com