Modeling of annealing kinetics for hydrogenated-amorphous-silicon-based solar cells using two-component metastable defects

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(Received 27 February 2006; accepted 2 May 2006; published online 14 June 2006)

We propose a kinetic model for the annealing in p-i-n-type hydrogenated-amorphous-silicon (a-Si:H)-based solar cells using a combination of the fill factor and “fast” and “slow” metastable defect states in their absorbers. Reported annealing data are simulated on p-i-n-type a-Si:H-based solar cells using the proposed model in order to confirm its validity. The recovery kinetic dependence on the thermal annealing temperature, biased voltage, and phase of the absorber controlled by the hydrogen dilution ratio during deposition are reviewed. Furthermore, we suggest a recovery mechanism for the solar cells based on long range hydrogen diffusion. © 2006 American Institute of Physics. [DOI: 10.1063/1.2213507]

Despite high interest of late in thin-film Si solar modules, a major obstacle to their commercialization remains. Specifically, light-induced degradation, which originates from the photocreation of dangling bonds (DBs) accomplished by the nonradiative recombination of photogenerated electron-hole pairs (Staebler-Wronski effect), limits the efficiency of hydrogenated-amorphous-silicon (a-Si:H)-based solar cells. In spite of extensive research on the Staebler-Wronski effect during the past 30 years, there is no consensus on a microscopic mechanism that explains all experimental phenomena. Similarly, the recovery mechanism for a-Si:H-based solar cells through thermal annealing or intense illumination at high temperature with a strong reverse bias has yet to be identified: the recovery kinetics against the circuit voltage and short-circuit current.2

The fill factor (FF) was selected 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 (i) absorber. (ii) Analytic equations relating FF to the collection length, i.e., \( \text{FF} \propto \mu \tau E \), where \( \mu \) and \( \tau \) are the average mobility and lifetime of photogenerated carriers and \( E \) is the internal electric field in the i absorber, and to the defect density (or electron spin density) have been developed.11 (iii) FF is the most degraded parameter against light soaking in a-Si:H-based solar cells8,12 and is less sensitive to the measurement temperature and illumination intensity compared to the open-circuit voltage and short-circuit current.2

\[ \text{FF} = \frac{N_i}{N_i + N_p} \]

where \( N_i \) and \( N_p \) are the defect densities in the degraded i absorber and the initial defect density in the i absorber, respectively. If we assume a two-component model having fast and slow metastable defect states \( N_i \) and \( N_p \), then \( N = N_i + N_p + N_{d1} + N_{d2} \). Furthermore, we assume that all the defects stem from a common pool of ground states, and there is otherwise no direct communication between the two defect components under fixed annealing conditions. In the case of thermal annealing, as the defect generation can be neglected, the rate equations for \( N_i \) and \( N_p \) can be expressed as the following simple first-order approximations,5

\[ \frac{dN_i}{dt} = -N_i / \tau_f \]

and

\[ \frac{dN_p}{dt} = -N_p / \tau_s \]

where \( \tau_f \) and \( \tau_s \) are time constants for the fast and slow metastable defects. Hence, \( N_i \) and \( N_p \) can be given by

\[ N_i = N_{d1} \exp(-t/\tau_f) \]

\[ N_p = N_{d2} \exp(-t/\tau_s) \]

After replacement of \( N \) and \( N_d \) by Eqs. (2) and (3), Eq. (1) becomes the following kinetic equation:

\[ \text{FF}_n = \ln[n(1 + \alpha \exp(-t/\tau_f) + \beta \exp(-t/\tau_s))] / \ln n, \]

where

\[ n = N_i / (N_i + N_{d1} + N_{d2}) = \exp[(\text{FF}_d - \text{FF}_f) / K_1], \]

\[ \alpha = N_{d1} / N_0 \]

\[ = \text{the photoreacted fast metastable defect density over the initial defect density,} \]

and \( \beta = N_{d2} / N_0 \) the photoreacted slow metastable defect density over the initial defect density. Therefore, we can fit thermal annealing behaviors using three independent parameters, \( \alpha \), \( \tau_f \), and \( \tau_s \).

Figure 1 displays the simulated results using the two-component kinetic model for the experimental results reported in Ref. 4. For comparison, we include the simulated results using the stretched exponential kinetic model given by

\[ \text{FF}_n = \ln[n + (1 - n) \exp(-t/\tau_{SE}^\gamma)] / \ln n, \]

where fitting parameters \( \tau_{SE} \) and \( \gamma \) are a time constant and a stretched

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exponential constant, respectively. The \( p-i-n \)-type solar cell was fabricated at \( \sim 200 \) °C via a plasma-enhanced chemical vapor deposition (PECVD) technique with a structure of glass/\( \text{SnO}_2 \)/hydrogenated \( p \)-type amorphous silicon carbide (\( p-a-SiC: \)H)/\( \text{H}_2 \)-diluted \( i-a-Si: \)H (\( \sim 300 \) nm)/\( n \)-type \( a-Si: \)H (\( n-a-Si: \)H)/ZnO/Al. In all measurements, the cell was degraded for 30 min under 50-sun illumination at 60 °C, and thereby FF\( _{i} \) and FF\( _{d} \) were always fixed at 0.67 and 0.56, respectively (\( n \approx 0.43 \)).

The recovery behaviors were inspected with the different biased voltages (\( V_\text{bi} \)) in the dark at a thermal annealing temperature (\( T_\text{d} \)) of 60 and 100 °C. From Fig. 1(a), it is clear that the two-component kinetic model fits the experimental data well in the last slow tail as well as the initial fast rise, compared to the stretched exponential kinetic model. Furthermore, the reported different recovery kinetics from identical FF\( _{i} \), which depend on the illumination intensity or temperature during the light-induced degradation, verify that the photocreation of DBs, that is lower than that for light-induced long range H diffusion (0.9 eV). Hence, the breaking of strong Si–H bonds (\( \sim 3 \) eV), proposed by Branz’s hydrogen collision model, 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 for the Staebler-Wronski effect. Recently, Powell et al. proposed the creation of two metastable HSiDB [complex of a DB and a Si–H bond, where H locates in a tetrahedral-like site (\( T_d \)), not a bond-centered site] defects; a H atom from a neighboring doubly hydrogenated weak Si–Si bond (HSiSiH) switches to a \( T_d \) site of the broken Si–Si bond and the other H from HSiSiH is also located in the energetically suitable \( T_d \) site. This model is acceptable because the spatial separation between H in the \( T_d \) site and DB is in agreement with the observed values of 4–5 Å by electron spin resonance (ESR) measurements.

On the other hand, it has been reported that the annealing of DBs in \( a-Si: \)H films, which are photocreated at moderate temperature, has a similar activation energy (1.1–1.2 eV) to that for long range H diffusion (1.5 eV). This supports the supposition that long range H diffusion plays an important role in the annealing of metastable defects. Thus, the hydrogen collision model is valid in the case of the annealing. In the current work, it is difficult to evaluate precisely the activation energy for recovery times due to the lack of the experimental data measured at various \( T_d \). Detailed study on the activation energy will be provided in further work. Nevertheless, as described by Carson and Rajan, \( E \) in a solar cell is expected to lower the energy barrier for long range H diffusion.

Based on the aforementioned models, we propose the following mechanism for the recovery kinetics for \( p-i-n \)-type \( a-Si: \)H-based solar cells. As a first step, mobile H is thermally emitted from a metastable HSiDB defect by breaking the Si–H bond. The elevated \( T_\text{A} \) increases the thermal emission rate of mobile H. The loss of bonded H is followed by weak Si–Si bond reconstruction. Meanwhile, mobile H migrates through the lattice and is subsequently captured at another weak Si–Si bond, which eventually forms a 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 Fig. 1(b), where \( \tau_{30} \) and \( \tau_{90} \) decrease due to the decrease in \( \tau_3 \) with a strengthened reverse bias. The thermal emission and recapture 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, considerable energy is required and a number of H atoms are involved. The classification between the fast and slow metastable defects is mainly determined by their energy level and capture cross section. However, this classification is only relative and is dependent on the annealing conditions, i.e., elevated \( T_\text{A} \) can significantly increase \( \alpha \).

The experimental recovery behaviors under 50-sun illumination with different \( V_\text{a} \) were also reported in Ref. 4. It was found that FF for the \( p-i-n \)-type \( a-Si: \)H solar cell recovered more rapidly under intense illumination at \( T_d = 70 \) °C with an increase in reversed \( V_\text{a} \). Therefore, 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.

Figure 2 shows the fitted results using the two-component kinetic model of the experimental recovery behaviors for the various $a$-Si:H-based solar cells reported by our group. The fitted results using the stretched exponential kinetic model are also included. A $p$-$i$-$n$-type solar cell was fabricated at 250 °C via a photoassisted chemical vapor deposition (photo-CVD) technique with a structure of glass/SnO$_2$/p-$a$-Si:H/i absorber (590 nm)/hydrogenated n-type microcrystalline silicon (n-$μ$-c-Si:H)/Al. Three different phases of $i$ absorbers were obtained via deposition with different hydrogen dilution ratios (H$_2$/SiH$_4$): (i) undiluted $i$-$a$-Si:H deposited at H$_2$/SiH$_4$ = 0; (ii) hydrogenated protocrystalline Si (pc-Si:H) deposited at H$_2$/SiH$_4$ = 1.5, which is located just before the threshold of the amorphous-to-microcrystalline transition;\(^9\) and (iii) for the $μ$-c-Si:H deposited at H$_2$/SiH$_4$ = 2.5. All the solar cells were degraded under four-sun, AM 1.5 illumination for 2 h at a temperature maintained below 50 °C by an air-cooling system. The FF values for the undiluted $a$-Si:H, pc-Si:H, and $μ$-c-Si:H solar cells are 0.71, 0.70, and 0.63, and the FF$_d$ values are 0.56, 0.58, and 0.53, respectively. The abrupt decline in FF$_d$ for the $μ$-c-Si:H solar cell reflects an inhomogeneous microstructure in $i$-$μ$-c-Si:H. It should be noted that the simulated data using the two-component kinetic model fit well for all the solar cells. In contrast, the stretched exponential kinetic model leads to an impossibly short $τ_{90}$ value and long tail. The $γ$ values for the undiluted $a$-Si:H, pc-Si:H, and $μ$-c-Si:H solar cells are 0.233, 0.208, and 0.221, respectively. The other fitting parameters and evaluated time constants are provided in Fig. 2; those for the two-component kinetic model are written in black, while those for the stretched exponential kinetic model in red. Among the solar cells, the pc-Si:H solar cell displays the rapidest recovery behavior due to having the highest $α$ and the shortest $τ_F$ and $τ_S$, which can be ascribed to the decreased structural disorder in the $i$ absorber by relaxing the $a$-Si:H matrix via the H$_2$ dilution of SiH$_4$ during the photo-CVD deposition.\(^{23}\) The unstable $i$-$μ$-c-Si:H at the onset of the microcrystalline regime\(^{24}\) can be attributed to the photocreation of DBs in defective H-rich grain-boundary regions formed between crystalline Si grains. At present, however, the slow recovery behavior cannot be clearly explained. The inhomogeneous microstructure in $i$-$μ$-c-Si:H may disturb the long-range H diffusion, causing a fluctuation of potentials in the band gap.

In conclusion, a kinetic FF annealing model for $p$-$i$-$n$-type $a$-Si:H-based solar cells employing fast and slow metastable defect states in their absorbers, as well as a recovery mechanism for the solar cells based on long-range hydrogen diffusion, were proposed. Our fits of the recovery kinetic dependence on $T_A$, $V_{st}$, and phase of the absorber controlled by H$_2$/SiH$_4$ during deposition are better than the fits using the conventional stretched exponential model. Since the stretched exponential method of fitting such recovery mechanisms does not parallel any physical phenomena, the proposed model can be deemed useful for limiting the number of mechanisms responsible for annealing the photocreation defects in $a$-Si:H.

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