The Limited Relevance of SWE Dangling Bonds to Degradation in High-Quality a-Si:H Solar Cells

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***Abstract*—Contributions of different light-induced defect states to degradation of solar cells have been established for high-quality p-i-n solar cells with i layers of protocrystalline a-Si:H deposited at very low rates, whose nanostructure is dominated by hydrogen-passivated divacancies. Nature of the different light-induced gap states and their respective roles as electron and hole recombination centers were characterized in the thin films from their photocurrents, and in corresponding solar cells from their Shockley–Reed–Hall carrier recombination currents. The results were directly related to three light-induced states, with "A" and "B" within 0.2 eV and "C" 0.4 eV below midgap, identified from subgap absorption. The A and B states are efficient electron, while the C states are very efficient hole recombination centers. Under 1-sun illumination, the former dominate the electron lifetimes, while the latter are key to solar cell operation as is confirmed by the direct correlation of their creation with the degradation of V_{OC} and 1-sun fill factor (FF). It is also shown that the apparent correlation found earlier between the cell FF and electron lifetimes is due to the same long-term degradation kinetics of the light-induced changes in the B t and C states.**

***Index Terms*—Amorphous silicon, defect states, light-induced degradation, photovoltaic cells, thin films.**

I. Introduction

THE Staebler–Wronski effect (SWE) and its role in the stability of a-Si:H solar cells are still important technological issues as the a-Si:H cells in tandem structures deliver two thirds and in triple junction structures one half of the expected power. Despite the extensive studies of SWE for nearly 40 years on different a-Si:H materials, there is no consensus about either its nature or the role that the light-induced defect states play in the degradation of solar cells. The vast majority of the studies on SWE, based on the view that isolated dangling bonds and their associated midgap states were solely responsible for the light-induced changes in a-Si:H, focused on issues that were related to the physical nature of such isolated dangling bonds as reviewed in detail by Fritzche [1]. In these studies, little attention was given to the nature of the light-induced changes in the gap states and carrier recombination responsible for the degradation of a-Si:H solar cells. Studies that did address these issues were fewer by far with little, if any, attention being given to their results [2], [3]. These results, however, did offer important insights into light-induced changes in carrier recombination and defect gap states that did not necessarily agree with the widely held "dangling bond" viewpoint, but are highly relevant to a-Si:H solar cell degradation.

Such results included: the extensive evidence for light-induced changes in gap states other than just neutral dangling bond midgap states [4]; two distinct regimes in the kinetics of light-induced changes in carrier recombination degrading under 1-sun illumination [2]; presence of "fast" and "slow" states [5], [6]; and changes in subgap absorption, $\alpha(h\nu)$, inconsistent with a single type of gap states and requiring presence of states away from midgap [7]. It is somewhat surprising that such results are overlooked or ignored in attempts, made even up to now, to explain the contribution of SWE to the degradation of solar cells [8]. In the studies that focused on the nature of light-induced states, and their contribution to the degradation of solar cells, unfortunately, it was not possible to reliably quantify the wide range of results. This was in part due to their being on porous and inhomogeneous a-Si:H, whose microstructural differences could not be adequately characterized. This limitation seriously affected the advances made in improving the stability of a-Si:H cells, because it led to an empirical approach based on just changing their deposition conditions. However, recently, Smets and van Sanden [9] developed a technique based on IR spectroscopy that is able to accurately characterize the nanostructure of a-Si:H. This offers the real possibility of developing a reliable method for relating the changes in SWE, to those in the microstructure, that could lead to a systematic improvement in the stability of a-Si:H solar cells. However, prior to this, it is important to establish the nature of the different light-induced gap states, with their role as both electron and hole recombination centers, so that their respective contributions to the degradation of solar cells can be evaluated.

Here, results are presented and discussed from a study addressing these issues, carried out on dense a-Si:H protocrystalline [10] thin films and corresponding solar cells whose nanostructure is dominated by divacancies [11]. Attention is given to the carrier recombination that is present under 1-sun illumination, which is the normal operating condition for solar cells. It is important to note that under these conditions, carrier recombination occurs not just through the midgap states, but a region of the gap that extends for about 0.9 eV. This study was able to characterize the nature of two states at and one away from midgap, identified with refined dual beam photoconductivity

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(DBP) measurements [12], as electron and hole recombination centers. It was then able to characterize the light-induced changes in them, including those in the fast states [13], and to directly relate them to the degradation of solar cell characteristics under 1-sun illumination.

II. Background

The vast majority of studies addressing SWE and light-induced changes were carried out on a-Si:H films consisting of a wide variety of porous undiluted a-Si:H whose microstructure was not well characterized, and no attempts were made to relate the results to solar cell degradation in a quantitative way. It is only recently that SWE studies were undertaken on dense, highly homogeneous, hydrogenated a-Si:H films and solar cells [2], [3]. Such a-Si:H exhibits not only significantly lower light-induced degradation but also under 1-sun illumination at 25 °C attains essentially a degraded steady state (DSS) after around a hundred hours rather than the many hundreds of hours. The studies reported here were carried out on such a-Si:H deposited in the protocrystalline regime [10] with high-quality solar cells as indicated by 1-sun fill factors (FF) of 0.73 in 4000 Å thick cells. It is also important to note that the p/i interfaces in these cells were such as to allow the carrier recombination to be dominated by that in the bulk i layers [14]. The approach taken in establishing the contribution of the different light-induced gap states to the degradation of the solar cells was first to establish their distributions in the gap and then to determine their role as *both* electron and hole recombination centers. To achieve this on the films, it was necessary to refine the DBP measurements and their analysis so as to be able to characterize the different states in detail and measure the electron mobility ($\mu\tau$) products up to 1-sun illumination.

It was also necessary to develop a method to characterize the light-induced gap states in solar cells, which is more direct than that available from the generally used degradation of FF. This was achieved by utilizing the ambipolar (electron and hole) Shockley–Reed–Hall (SRH) recombination in the diffusive currents of the cells under forward bias. This approach was particularly useful in these high-quality cells because of relatively homogeneous low densities of states across the i layers and the low potential barriers confined close to the n and p contacts that lead to essentially a uniform field across the i layer [14], [15].

In detailed studies on carrier transport and carrier recombination mechanisms in cells such as studied here, using an analytically derived model, Deng and Wronski [14] were able to show how the voltage-dependent diode quality factors, $n(V)$, in the forward bias, $J_D - V$, characteristics depend on the densities of states and their conversion into recombination centers with the quasi-Fermi (QF) splitting equal to the applied voltage V. They were was also able to explain the presence of the superposition of the short-circuit current–open-circuit voltage ($J_{\rm sc}-V_{\rm oc}$) and the dark current (J_D-V) characteristics over extended regions of current and voltage [15]. This was possible even though the superposition principle, such as exists in the case of c-Si cells, does not apply, since the photocurrents in a-Si:H are not diffusive but field driven and thus voltage dependent. In addition, this model could explain, by separating the contributions of the field-driven transport of photogenerated carriers from the diffusive currents, how the solar cell characteristics in these cells depend on bias and the introduction of light-induced defect states. This methodology was adopted in this study rather than relying on a numerical model where fitting to the experimental data on solar cells involves a large number of unknown and adjustable parameters.

The more direct method of characterizing the light-induced gap states based on SRH recombination allowed the carrier recombination originating from different regions of the gap to be probed by changing the QF splitting equal to the applied voltage. This enabled quantitative correlations to be made between the SRH carrier recombination in cells with the photocurrent recombination in corresponding films and reliable, detailed information to be obtained about the nature of the different light-induced gap states. As a consequence, it was possible to establish the individual contributions of the different defect states directly to the light-induced changes in the thin films and solar cell characteristics, as well as solar cell degradation under 1-sun illumination.

III. Experimental Procedures

The p-i-n superstrate solar cell structures in this study were in the form of glass/specular SnO_2/p a-SiC:H (250 Å)/i a-Si:H (4000 Å)/μc-Si:H (350 Å)/1000 Å Cr fabricated in a multichamber system using RF plasma-enhanced chemical vapor deposition under conditions previously described [16]. The intrinsic layers consisted of protocrystalline a-Si:H obtained with dilution $R = 10$ ($R = [H_2/SiH_4]$ deposited at 0.55 torr, low power, and very low deposition rate of 0.5 Å per second. To control the recombination in the p/i interfaces the i layers were also deposited with a two-step process previously described [17]. The p-SiC:H and n μc-Si:H contacts were of sufficiently high quality as to give under 1-sun illumination an open-circuit voltage of 0.93 V with the i layer bandgap of 1.8 eV. To minimize any external contribution to the J_D-V characteristics at low voltages, small areas (2 mm^2) were defined by the evaporation of the Cr through a shadow mask with subsequent etching off to uncover the n μc-Si:H layer. To eliminate the contributions of external resistance to the cells at higher voltages, a three-probe technique was used, in which two probes on the Cr and ITO contacts of the cells allowed the currents and the voltages to be measured through separate electrical paths. The current–voltage characteristics were obtained with computer-controlled measurements with 25-meV steps with excellent reproducibility in J_D-V characteristics being obtained for different cells on the same substrate.

The procedures in this study also took into account the RT annealing in midgap states [13] and ensured that direct correlations could be made between the results on thin films with those on the corresponding cells. In the characterization of thin films, care was taken to measure the electron $\mu\tau$ products accurately up to 1-sun illumination by having $n^{\pm}$ a-Si:H ohmic contacts in the coplanar structures and careful monitoring of the different carrier generation rates. To take account of the "fast" states in

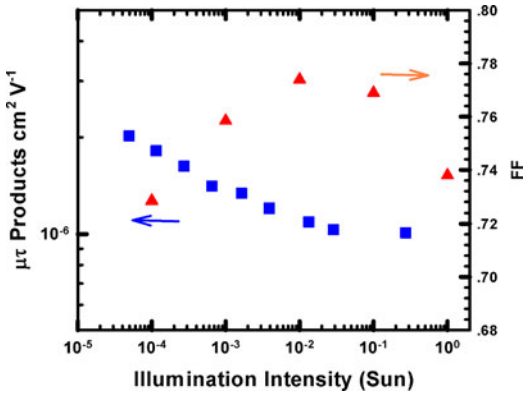

Fig. 1. The film electron $\mu\tau$ products and the corresponding fill factor (FF) in an annealed 4000 Å p-i-n solar cell as a function of illumination intensity up to 1 sun. Observe the inverse behavior of $\mu\tau$ and FF during an increase in Quasi Fermi level splitting.

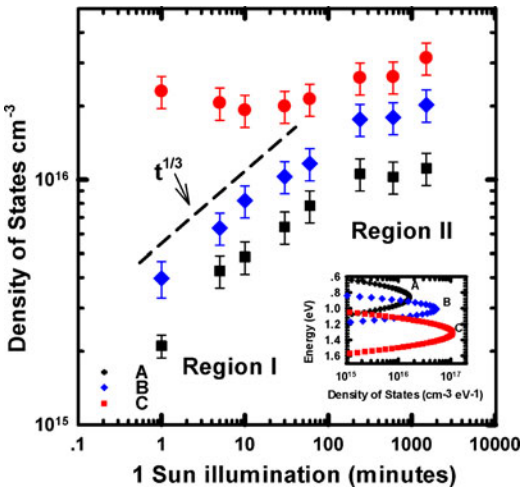

Fig. 2. The light induced changes in the densities of the A, B, and C states, during 1 sun degradation at 25 °C, obtained from subgap absorption measured with DBP. In the inset are the energy distributions of these states shown relative to the conduction band.

the subgap absorption measurements these were not carried out under continuous with 1-sun illumination. Rather a sequence of longer and longer degradations with annealing out of the created light-induced defects prior to subsequent illumination. The reproducible annealed states of the films were obtained after annealing them at 170 °C for 4 h. The derivatives of the DBP measurement results were fitted with three Gaussians, the presence of which was indicated in the self-consistent fitting of previous results on a-Si:H films [4].

In solar cells, the carrier recombination was not characterized with just solar cell characteristics but was also measured directly with SRH recombination. The regions of the gap where the states act as recombination centers were defined by controlling the QF splitting with, intensity of illumination in film photoconductivities, and forward bias in SRH measurements. Such QF splitting enabled the contributions to carrier recombination of different states to be characterized for electron $\mu\tau$ products from photoconductivity and holes from SRH measurements. Because of the large number of the 2-mm^2 cells on any given substrate, it was possible to carry out a new set of experiments on any given cell without having to anneal out any prior degradation.

IV. Results and Discussion

The contribution of the continuous distribution gap states in a-Si:H to carrier recombination in these films and solar cells was addressed in the annealed state by selectively converting the gap states, at and away from midgap, into recombination centers by increasing the QF splitting with the level of illumination [18]. Fig. 1 shows the results for the electron $\mu\tau$ products obtained from the photocurrents in an a-Si:H film as the illumination is increased up to the level of 1 sun. Also shown are the corresponding results for the FF of a 4000 Å p-i-n solar cell up to 1-sun illumination with a QF splitting of 0.93 eV. There is a striking contrast between the results for electron lifetimes, τ_n, and those of the FF which is determined primarily by the hole lifetimes, τ_p. In the case of the films, there is the generally observed decrease in τ_n with illumination, but in addition there is a clear absence of any further decrease once the QF splitting reaches the value generated by $\sim 10^{-2}$ sun. This shows that the additional states introduced away from midgap do not act as efficient electron recombination centers as τ_n remains determined by what may be called midgap states.

The results on the FF and, consequently, on τ_p indicate quite an opposite role for the two sets of gap states. While the midgap states act as recombination centers, the FF increases with illumination, as is the case for c-Si cells [19], indicating that introduction of these recombination centers has a small perturbation on hole lifetimes. However, after reaching the $\sim 10^{-2}$ sun illumination, the states away from midgap become hole recombination centers; the FF begins and then continues to decrease. This is a clear indication that those states, which have negligible effect on τ_n, have large hole capture cross sections that limit the FF under 1-sun illumination. The results also clearly show that the midgap states, which for a long time have been recognized as efficient electron recombination centers, have a very much smaller effect on holes than the gap states located away from midgap.

These two sets of gap states and their light-induced changes in the a-Si:H films were identified in a detailed study carried out by Niu [12] who characterized their subgap absorption spectra with DBP and analysis that took into account the presence of multiple defect states. In these studies, where the states that anneal out at room temperature were taken into account, three different Gaussian distributions were identified from the derivatives of $\alpha(h\nu)$. In this a-Si:H with the bandgap of 1.8 eV, there are two states at midgap, A at 0.05 eV above and the B at 0.095 eV below midgap, with the third C states 0.39 eV below midgap. The energy distributions of these three gap states after 30 min of 1-sun illumination at 25 °C are shown relative to the conduction band in the inset of Fig. 2. In this a-Si:H, with a bandgap of 1.8 eV, the peaks of the Gaussians relative to midgap are: A at 0.05 eV above; B at 0.095 eV below; and C at 0.39 eV below. Since the A and B states are located very close to 0.9 eV below the conduction band, they can be termed as the "midgap" states. Even though the C states are close to the valence band tail, it

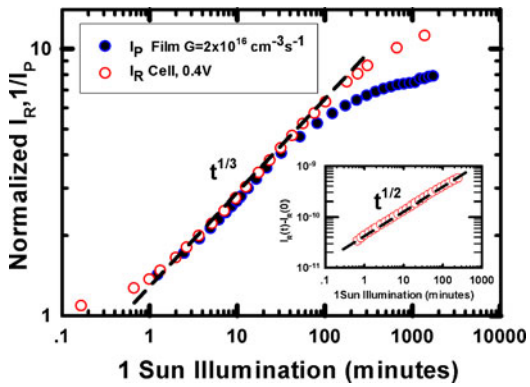

Fig. 3. The SRH recombination current, I_R, and the corresponding inverse of the normalized film photocurrent, I_P, for Quasi Fermi splitting of 0.4 eV during 1sun illumination at 25 °C. The inset illustrates how the $t^{1/3}$ time dependence of the increase in the A and B states reflects a $t^{1/2}$ dependence for their creation rate. R

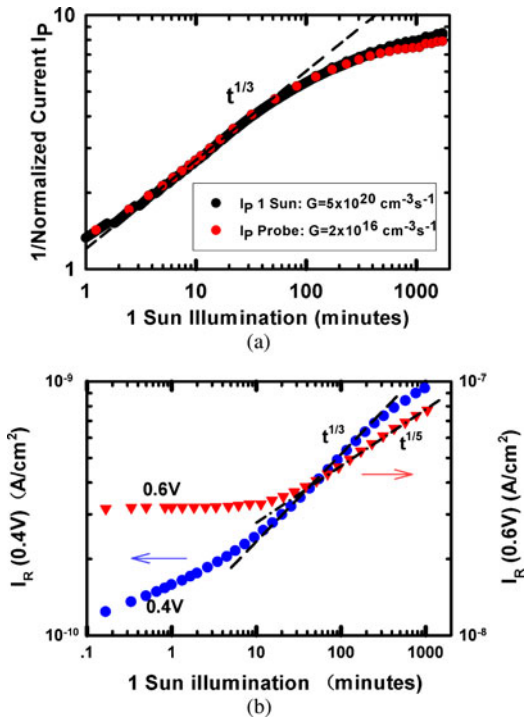

Fig. 4. (a) The inverse of the normalized 1 sun film photocurrents, I_R, with carrier generation rates of 2×10^{16} and 5×10^{20} cm^{-3} s^{-1} during 1 sun degradation at 25 °C. (b) The Shockley-Reed-Hall (SRH) recombination current, I_R, for QF splitting of 0.4 and 0.6 eV during 1 sun illumination at 25 °C. The former is with just A and B states while the latter is when C states are also present as recombination centers.

was possible to clearly separate them and their evolution from the exponential distribution of the tail states.

During the degradation, the increase in the areas under the Gaussians occurred with very little or no change in their peak energies or half widths. The changes in the respective electron-occupied states, which are obtained from the areas under the Gaussians, are shown in Fig. 2 for a bias illumination of 1 nA. These changes reflect those present in the actual densities of states as the kinetics of the changes are found to be independent of the bias illumination. It can be seen in the figure that in the time frame of the experiments, the changes in the three distributions of states are distinctly different. Nevertheless, all of them exhibit two regimes, I and II, with transitions between the two occurring after about a half hour of illumination. In regime I, there are large increases in both the A and B states, while there is no increase in the C states. Also shown in Fig. 2 is a guide to the eye time dependence of $t^{1/3}$, one that is extensively reported for light-induced changes in a-Si:H photocurrents. On transitioning into regime II, there is no longer any increase in the A states, reflecting their nature as the fast states that anneal out even at 25 °C [13]. On the other hand, the B states now increase at a slower rate which is similar to that for the onset of the increase in the C states.

The role of these states as recombination centers was characterized by selectively converting them into recombination centers by increasing the QF splitting. In the case of the films by changing the carrier generation rates for the photocurrents, I_P, from 5×10^{15} to 5×10^{20} cm^{-3}·s^{-1}, and in the case of cells by changing the forward bias for the SRH recombination currents, I_R, from 0.3 to 0.6 V. These results could be directly related to three gap states in Fig. 2 and applied to characterizing them as electron and hole recombination centers. Fig. 3 shows the results of 1-sun degradation at 25 °C for the cell SRH recombination currents, I_R, at 0.4 V forward bias and the inverse of the film photocurrents, I_P, with a similar QF splitting. The two results correspond to the recombination through the A and B states. Even though I_P depends solely on τ_n and I_R on both τ_n and τ_p, the excellent superposition in the kinetics of their changes clearly shows that they reflect the same creation of midgap states in the films and solar cells.

The kinetics of these recombination currents clearly exhibit a $t^{1/3}$ time dependence, such as indicated in Fig. 2 for the A and B states, with a transition into the regime II that leads to a DSS after about 100 h. It should be noted here that this $t^{1/3}$ kinetics seen here and in Fig. 2 are for the *increase* in the total densities of the A and B states. As such it does not, as is generally assumed, reflect the actual *creation rate* of the light-induced gap states which can be obtained only after the density of states prior to the degradation is taken into account. This is illustrated in the inset of Fig. 3, where the difference between SRH current at time t, $I_R(t)$, and the initial value, $I_R(0)$, are shown as a function of the 1-sun illumination time. It can now be clearly seen that the time dependence for the actual *creation* rate of the A and B states is $t^{1/2}$ and not $t^{1/3}$. It is important to note that this time dependence holds even when the density of the created states is smaller than that of the intrinsic states, as found in the extensive studies on the creation of metastable defect states in this a-Si:H [20].

There is, however, a striking difference between the kinetics of these two recombination currents when the QF splitting is increased so as to introduce the C states as recombination centers, as illustrated in Fig. 4. In Fig. 4(a), the inverse of the normalized I_P photocurrents are shown for carrier generation rates of $G = 2 \times 10^{16}$ and 5×10^{20} cm^{-3}·s^{-1}. In this case, the intensity dependence of the $\mu\tau$ products during degradation

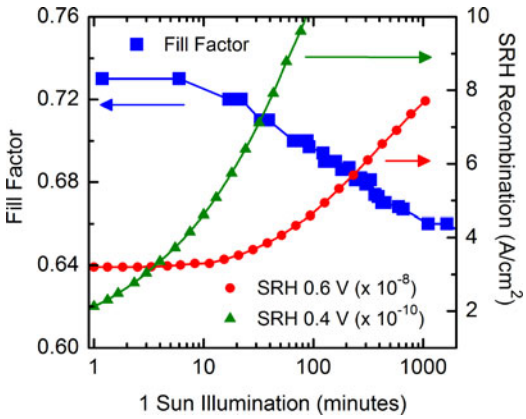

Fig. 5. Changes in the 0.4 V and 0.6 V SRH recombination currents and the 1 sun FF during 1 sun illumination at 25 °C.

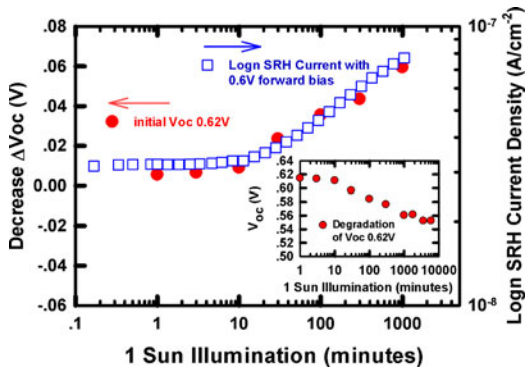

Fig. 6. The inset shows the decrease in the initial $V_{\rm OC}$ of 0.62 V during degradation with 1 sun at 25 °C. The figure illustrates the direct correlation between the decrease in $V_{\rm OC}$, $\Delta V_{\rm OC}$, and the logarithm of the SRH recombination with 0.6 eV Quasi Fermi splitting.

remained quite similar to that in the annealed state, with intensity-independent values at the high generation rates, when the C states are included as recombination centers. The identical $t^{1/3}$ time dependence in the changes of the photocurrents, when the generation rates change by 10^5, is a clear indication that the electron lifetimes in both cases are dominated by the A and B states. This, just as prior to degradation, shows that the C states are inefficient electron recombination centers so that the light-induced midgap states determine τ_n even at 1-sun illumination. In Fig. 4(b), the SRH recombination currents are shown for the QF splitting of 0.4 and 0.6 V forward bias. In this case, a dramatic change occurs in the kinetics of the SRH recombination currents when the C states are introduced as recombination centers with the QF splitting to 0.6 eV. In this case, the changes in the SRH recombination currents closely follow those of the C states in Fig. 2. There is still the striking absence of any changes during the large $t^{1/3}$ increase of the midgap A and B states in region I, but here the transition into region II can now be clearly identified to have a $t^{1/5}$ time dependence. It is important to remember that even though the C states cannot be detected in electron photocurrent recombination, they can, with SRH ambipolar recombination, be determined by both τ_n and τ_p. Because of their large hole capture cross section of their introduction recombination centers, the SRH currents become dominated by τ_p, rather than τ_n,when carrier recombination occurs through only the A and B states. The differences in the kinetics of the light-induced changes in the A, B, and C states, as well as in their nature as recombination centers, offer fingerprints for their respective contributions to the degradation of solar cells under the 1-sun illumination.

Under this illumination, both the A, B midgap and the C states contribute to the degradation of the solar cells. Results are presented in Fig. 5, where the contribution of A and B states to the degradation of the 1-sun FF can be separated from that of the C states. The figure shows the changes under 1-sun illumination in the SRH currents of just the A and B states, J_R with 0.4 V, as well as when the C states are included as recombination centers, J_R with 0.6 V. Also shown is the corresponding 1-sun FF which exhibits two sets of degradation rates. It can be seen that when initially there is large increase in the A and B states and no change in the C states, there is virtually no change in the FF. On the other hand, as soon as there is an increase in the C states, as expected from their effect on τ_p, there is the onset of degradation in the FF.

A more direct and quantitative correlation can be found between the increase of the C states and the degradation in the cell open-circuit voltage, $V_{\rm OC}$. In these 4000 Å thick cell structures with the protocrystalline a-Si:H i layer, there was virtually no decrease in the 1-sun short-circuit currents, $J_{\rm SC}$, even after degradation to a DSS with 1 sun at 25 °C. The $J_{\rm SC}$ was generated with one pass absorption in the i layer, with minimal reflection from the Cr back contact, and no optical enhancement from the specular CTO. As indicated earlier, in the detailed study on the $J_{\rm sc}-V_{\rm oc}$ characteristics over a wide range of illumination, Deng *et al.* [15] found that in these a-Si:H cells, superposition of the $J_{\rm sc}-V_{\rm oc}$ and the dark current J_D-V characteristics was present over extended regions of current and voltage. They then showed that the superposition is present if $J_D = J_{\rm diff} > J_{\rm RG}$, where $J_{\rm diff}$ is the diffusive forward bias current and $J_{\rm RG}$ is the current corresponding to the recombination of the photogenerated carriers in the bulk i layer. Superposition between $J_{\rm sc}-V_{\rm oc}$ and J_D-V, however, will not be present if at $V = V$oc, $J_{\rm RG}$ is comparable with or larger than $J_{\rm diff}$, and under these conditions, Voc cannot be related to the SRH recombination currents. Even though superposition is present to high values of voltage, the introduction of light-induced defect states and corresponding increases in $J_{\rm RG}$ can limit such superposition and direct correlation to SRH recombination currents J_D to lower and lower values of Voc.

The inset of Fig. 6 shows the 1-sun degradation in $V_{\rm oc}$ of 0.62 V which also exhibits two regimes similar to those of the FF in Fig. 5. In this case, the QF splitting is close to 0.6 eV; therefore, its light-induced changes should correspond to those in the J_D at 0.6-V forward bias in Fig. 4(b). At this voltage, it is possible to directly relate the light-induced changes in $V_{\rm OC}$ to the those in the bulk C states since $J_D \gg J_{\rm RG}$, as confirmed by the presence of the superposition characteristic even after 10 h of the 1-sun degradation at 25 °C. Fig. 6 then illustrates the decrease, $\Delta V_{\rm OC}$, in this voltage under 1-sun illumination at 25 °C as well as the SRH recombination at 0.6 V such as

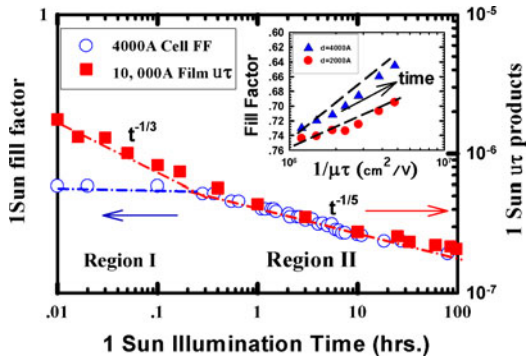

Fig. 7. The inset shows the correlation between the 1 sun FF of p-i-n solar cells with different thickness and the corresponding film $1/\mu\tau$ products, both in region II of 1 sun degradation at 25 °C. The figure shows separately that the 1 sun FF and $\mu\tau$ products where in region II both have the same $t^{-1/5}$ time dependence that leads to the results shown in the inset.

seen in Fig. 5. Excellent superposition can be seen in the figures between $\Delta V_{\rm OC}$ and the change in J_D(0.6 V), which is plotted on a logarithmic scale since $V_{\rm OC}$ has a logarithmic dependence on J_D [15]. This quantitative agreement between the change in the C states, as indicated by J_R(0.6 V), and $V_{\rm OC}$ clearly shows the absence of any significant contribution from the light-induced midgap states to cell degradation under close to or at 1-sun illumination.

In analyzing the kinetics in region II of the degradation under 1-sun illumination on protocrystalline films and cells such as those here, Pearce *et al.* found what appears to point to midgap states being responsible for the degradation of the 1-sun FF [3]. This was indicated by the apparent direct correlation between the changes in the midgap states, known to be efficient electron recombination centers that determine the electron $\mu\tau$ products, with those in the 1-sun FF. Such correlations are shown in the inset of Fig. 7, where the 1-sun FF for two cell thicknesses is plotted versus $1/\mu\tau$ during period of about 100 h in region II.

In Fig. 7, the changes in the 1-sun FF and the electron $\mu\tau$ products in films are shown separately with the transitions in their kinetics clearly visible. In region I, there are the previously discussed kinetics of $\mu\tau$ and FF changes that result from the creation of the A, B, and C states. In region II, it can now be seen that the previously seen initial changes in the C states, with a $t^{1/5}$ time dependence, continue as such over the 100 h or so it takes to approach a DSS. This is reflected in the changes of the FF having the time dependence of $t^{-1}/5$. What is new and somewhat surprising in Fig. 7 is the result for the time dependence of changes in the $\mu\tau$ products in region II which is also $t^{-1}/5$. Since in this region the $\mu\tau$ products depend solely on the B states, this points to the changes in the B and C states having the same time dependence. It is such a time dependence, and not the contribution of the midgap B states to hole recombination, that leads to the results in the inset of Fig. 7. It is, therefore, not surprising that without a detailed knowledge about the nature of the different light-induced gap states, a misconception would arise about the importance of midgap states in the degradation of solar cells even operating under 1-sun illumination.

V. Conclusion

The results presented here clearly demonstrate that the degradation in these cells operating under 1-sun illumination is determined by the light-induced changes in C states located 0.4 eV below midgap, with the A and B states within 0.2 eV of midgap having a negligible effect. Under 1-sun illumination at 25 °C, the changes in the gap states exhibit two regimes, with regime I transitioning after about half an hour into regime II which leads to essentially a DSS after around 100 h. In regime I, the A and B states exhibit the same $t^{1/3}$ time dependence for their light-induced changes, while there is no increase in the C states. However, in regime II, while there is no longer any further increase in the A states, the B and C states change with a $t^{1/5}$ time dependence. It is this same time dependence for the changes of the B and C states in regime II, and not the contribution of the midgap states to hole recombination, that leads to a correlation between electron $\mu\tau$ products and FF [3]. A lack of any contribution from the A and B states, and the importance of the C states, to the degradation of the solar cells was clearly identified from their respective effect on the 1-sun FF. On the other hand, the dominant role of the light-induced C states is demonstrated with the quantitative correlation between their increases and the degradation in $V_{\rm oc}$. Evidence for the two regimes and a $t^{-1}/5$ time dependence in the degradation of Voc were also reported by Liang *et al.* [21]. They attributed such results to carrier recombination through both the tail states and light-induced midgap states. However, it is shown here that the degradation in cell characteristics under 1-sun illumination is determined solely by the light-induced changes in the clearly identified C states.

From the correlation of the results on the electron photocurrents in films and the ambipolar SRH currents in cells, it was possible to obtain insights into the nature of the different states. In this dense protocrystalline a-Si:H, clearly the A states are the fast states [2], [13] for which no evidence was found in 1-sun degradation of the porous a-Si:H films. The very large changes in the $\mu\tau$ products upon their relaxation at RT point to larger electron capture cross sections, S_n, than those for the B states. Despite the large difference in the rates at which the midgap states in the dense and the porous a-Si:H films are created under 1-sun illumination, there are some similarities between the midgap B states and those that have been generally associated with dangling bond D^0 states. This includes their $t^{1/3}$ initial increases and their annealing out at temperatures above 100 °C. In both cases, the states are efficient electron recombination centers and capture cross sections associated with a neutral recombination centers [4]. It is also interesting to note that kinetics of 1-sun light-induced changes similar to those in the B states have been seen in the ESR signal, generally associated with isolated dangling bonds [22].

Evidence pointing to states below midgap, such as the C states clearly identified here, had been found from the self-consistent fitting of different results on thin films using numerical modeling. This could only be obtained using similar three Gaussian distributions and with negatively charged states below midgap [23]. Such C states have very small electron and very

large hole capture cross sections that would explain their complete lack of effect on the electron lifetimes and the dominant role in determining the hole lifetimes.

Despite some similarities of the B states to the gap states that are considered to be due to isolated dangling bonds, the states discussed here are associated with divacancies [11], [24], [25]. This is because not only in this dense, a-Si:H is the nanostructure dominated by their presence, but also because of the similarity in the separation in the gap state distributions to those of the defect states in crystalline divacancies [26]. Consequently, in addressing the origin of SWE defects in dense protocrystalline a-Si:H, it is necessary to consider mechanisms related to divacancies [27], [28] rather than just isolated dangling bonds. They must also take into account that the actual creation rate of the defects responsible for midgap states is $t^{1/2}$ and not $t^{1/3}$ as has been generally assumed.

It should be mentioned that in the case of the divacancies in crystalline silicon, there are four sets of gap states; therefore, it may be possible that there is a fourth set of states in the a-Si:H. States, such as those reported to be 0.5–0.6 eV from the conduction band [29], would not have been detected here because of the limitation in the DBP measurements. However, such states would not be "midgap" since they would become recombination centers only at illumination levels similar to those required for the C states.

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