The stability of solar cells is a key factor in determining the reliability of photovoltaic modules and is of great interest in the case of solar cells having a new technology which has not yet been fully developed. In particular this question arises with hydrogenated amorphous silicon (a-Si) solar cells because a-Si exhibits reversible light-induced changes in its electronic properties, commonly referred to as the Staebler-Wronski effect (SWE).

Continuous progress is being made in the peak conversion efficiencies of a-Si solar cells and efficiencies in excess of 11% have been achieved. This progress results from the continuous improvements made in material synthesis, device processing as well as the introduction of new device structures. This makes it difficult to obtain a detailed evaluation of the effects that light-induced changes in a-Si have on the degradation of solar cell efficiencies. Furthermore because of the time required to characterize the long term stability of solar cells there are relatively few results reported on high efficiency cells. The results however clearly show that stability is still a problem, even though efficiencies to which the devices degrade have significantly improved. Recently, ARCO Solar has reported results on solar cells which, after over a year's exposure to sunlight, under open circuit conditions, still had about 7% conversion efficiency(1). These results by Ullal et al. are shown in Figure 1. The data in Figure 1, as well as that reported by others, exhibit a region of fast degradation for about a month but that the degradation then becomes very slow.
The large changes that occur quite rapidly, which have been and are being studied quite extensively, are found to be reversible. These light-induced changes in cell performance are generally associated with the SWE rather than changes in the junctions, interfaces and contacts. The light-induced changes associated with SWE occur: in the bulk of the a-Si, they occur with sunlight illumination; they are perfectly reversible upon annealing in the dark at ~200°C; and they result from the introduction of metastable defect. Such changes occur in undoped and doped a-Si films which have been prepared under a wide range of preparation conditions.

The reversible-light induced changes in a-Si were first observed and characterized by the decreases in the dark conductivities and photoconductivities of a-Si films(2). Figure 2 and 3 show the decreases in dark conductivity (dashed lines) and photoconductivity (solid lines) for glow discharge produced a-Si films during illumination with 200 MW cm⁻² filtered tungsten light. Figure 1 is for an undoped a-Si film and Figure 2 is for an a-Si film doped with 0.1% PH₃(3).

As can be seen in these figures the changes in the dark and photoconductivities can be very large (orders of magnitude) and they occur rapidly upon illumination comparable to 1 sun. Consequently such changes are still used to characterize the presence of light-induced changes in a-Si. However it should be pointed out here that since the changes result from the introduction of metastable defects into the gap of a-Si, the effects of such defects depend strongly on the densities of the initial states in the gap as well as the type and densities of the light-induced defects with larger densities of gap states the conductivity changes may become smaller or even not detectable. Correspondingly solar cells that have low efficiencies to begin with may have much smaller degradation. It
is important also to note here that the changes in conductivities exhibit quasi-exponential decays that depend on the light intensity and which at illuminations of ~1 sun may have time constants of the order of 10 hours.

The continuous introduction of the metastable defects leads to continuous changes in the lifetimes of photogenerated carriers. This is illustrated in Figure 3 where the photoconductivity $\sigma_p$, generated by penetrating light is shown as a function of relative light intensity for the undoped a-Si film of Figure 1 after annealing and subsequent prolonged exposure to light to a maximum of 4 hours$^2$. These changes indicate that the introduction of metastable defects not only decreases the electron lifetimes but also changes the kinetics of recombination.

The large changes in kinetics seen here illustrate that the extent of the light-induced photoconductivity change depends on the level of illumination. This is important to keep in mind when considering changes in solar cell performance. Because of the device nature of solar cells their recombination kinetics are more complicated and involve both electron and hole lifetimes. The effect of introducing metastable defects on the recombination of carriers will depend both on the type of illumination as well as the device structure itself.

The changes in dark conductivities and photoconductivities are found to be perfectly reversible upon annealing in the dark at temperatures ~150 to 200ºC. Because the defects are metastable the rate at which they anneal out depends on the temperature. This is illustrated in Figure 4 where the thermal relaxation time is shown as a function of temperature. The measurements were made at the indicated temperatures as shown in the inset where the slope of the line gives an activation energy of 1.5 eV$^2$. There is a lack of systematic studies in which the temperature of
the light-induced changes and kinetics of the annealing process have been investigated. However the results shown in Figure 4 indicate that the operating temperatures of solar cells are important in determining light-induced changes of their performance.

There have been many studies carried out on the reversible degradation in a-Si solar cell characteristics. These studies have been carried out on a-Si materials fabricated under different conditions, materials that contain different types and levels of impurities and defects as well as on solar cells having different device structures. A wide range of results are reported not only on the changes in cell efficiencies but also in the different cell parameters. This wide variation is due to both the different materials and the different device structures used. The cell structures are important because even with the same materials they can be used to modify the recombination kinetics. This changes both the rate at which metastable defects are created as well their effect on the overall characteristics (4). Because of this wide range of results it is difficult to quantify the relations between metastable defects and the light-induced changes in the cell parameters. In general degradation, to a varying degree, occurs in all three cell parameters.

The open circuit voltage appears to be the least sensitive to light-induced changes but significant degradations can be found especially after long exposures. Some of these changes however are not reversible which would exclude the SWE as the principal cause. Changes in the short-circuit currents are the primary causes of light induced degradation in a-Si solar cells.

The short-circuit currents are affected by the introduction of metastable defects because their effect on the carrier lifetimes and the
electric field distribution in the cell. As indicated earlier this effect depends strongly on the device structure as well as the types and densities of light-induced defects which are likely to be different for cells fabricated under different conditions. The contribution of changes in the hole lifetimes and the electric field which lead to changes in the short-circuit currents are illustrated in Figure 5. The results in Figure 5 show the change in the spectral response of a Pt/thick a-Si solar cell structure in annealed state A and light soaked state B (30 hours of AM1 illumination). In these simple cell structures the increase in the short-wavelength response results from an increase in the surface electric field and decrease at the longer wavelengths results from the shorter hole lifetime and diffusion length. It should be pointed out here that the difference in both the magnitude and spectral response are obtained even with these simple cell structures which result from relatively minor changes in the fabrication of the a-Si and it has been difficult a-priori to predict either the rate of the degree of degradation in the short-circuit current. It is also important to note here that the changes in hole lifetime significantly smaller than the electron (photoconductivity) lifetimes have also been observed, indicating that light-induced defects can be created which are quite different to those initially present in the a-Si.

Because the fill-factor is the cell parameter that is most sensitive to both carrier lifetime and electric field changes, it is also most sensitive to the a-Si material and the cell-structure. It is therefore the most difficult to characterize its changes in terms of light-induced defects particularly since there are such large uncertainties about the exact nature of these defects. Unfortunately it is the cell parameter that often dominates the degradation of high efficiency a-Si solar cells.
Despite the large number of studies on light-induced degradation of cell efficiencies and cell parameters there have been very few studies where these changes have been directly related to the light-induced defects whose densities and electronic properties have been measured using different techniques. Furthermore even though light-induced changes in a-Si have been of interest since 1976 these changes are still not well understood. Although there is general agreement that these changes result from the introduction of metastable defects there are still many unanswered questions regarding their origin, nature and electronic properties. It is not yet known how many different metastable defects can be created in a-Si, if there is a single type of defect that is dominant in high quality a-Si, whether the defects are related to impurities, dopants or just structure and what is the electronic nature of these defects.

The answer to such questions and the control of these defects are clearly necessary before it is possible to accurately project their ultimate limitation on the long term performance of high efficiency a-Si cells. The present lack of these answers means that great care must be taken in evaluating the degradation in a-Si solar cells and modules.


Figure 1

Sunlight Exposure
p-i-n, TF Si:H (6 Cells)
A = 4 cm²
△ Experimental
— Computed

Efficiency (%) vs. Time (Days)

Ullal, Morel, Wilet, Kanani

STAEBLER-WRONSKI EFFECT
Figure 2

CONDUCTIVITY (Ω·cm)$^{-1}$

-3
-4
0
10
20
30
40
50

-7
-8
-9

0 100 200 300 400 500

TIME (MIN)

ILLUMINATION

0.1% PH$_3$

DARK $\sigma$

A
Figure 3

Conductivity (Ω·cm)^{-1}

Time (min)

Illumination

Undoped

Dark $\sigma$

22
Figure 4

Relative Intensity, $F$

$\sigma_p (\Omega \cdot cm)^{-1}$

$\gamma = 0.5$

Annealed

$\gamma = 0.89$

Exposed 4 Hours
Figure 5

The graph shows the relationship between temperature and optical exposure. The temperature is plotted on the x-axis, while the optical exposure is plotted on the y-axis. The graph includes markers for temperatures of 190°C, 180°C, 170°C, 160°C, and 150°C, with arrows indicating the temperature changes. The y-axis is labeled with log scales, ranging from 10 to 10^4. The x-axis is labeled as \( \frac{1}{(1000/K)} \) and ranges from 2.15 to 2.35. The inset shows a time vs. \( \sigma \) plot, with a shaded region indicating optical exposure.
Figure 6

Collection Efficiency vs. Wavelength (μm)

- State A
- State B
Figure 7

Bias Illumination $10^{-2}$ Suns

- State A
- State B

$(\alpha E)^{3/2}$ (cm$^{-1}$ eV)$^{3/2}$ vs. Energy (eV)
DISCUSSION

KIM: Do you think that some of the defects are created by laser scribing or some other processing?

WRONSKI: Certainly, but I suggest you ask ARCO and Solarex, Thin-Film Division. Any light-induced stress obviously is going to cause an effect. The other question is what energy has the light used. If you use a laser scriber with a short wavelength you will damage the surface region of the junction. It doesn't seem to be wavelength-dependent, providing you can create the photogenerated carriers, which can be done quite efficiently even with sub-band-gap light. It is the recombination of a hole and an electron. You need a lot of recombination before you get one defect.

HERWIG: Presumably some wavelength would be more active in creating interaction with the impurity that some other wavelength --

WRONSKI: That is correct. The detailed studies have not become reality. There is a lot of work to be done. It is very important for people to get together and exchange their experiences, as this field is completely open.

LESK: I wonder whether these cells behave like crystalline silicon, in that if it's space charge recombination-dominated you get a large $E'V/2kT$ term. You blame some of the effects on recombination. Do you see, under forward bias, a large increase in the $2kT$ term, or do they behave differently?

WRONSKI: All I can talk about is the Schottky barrier; that's the one we have really studied. The results I've shown here are trying relate the bulk. In order to get at the bulk we try to minimize any effect of a p junction, of cell thickness, and so on. Yes, you do get a degradation, you do get a change in the diode quality factor.

LESK: The bulk is the high region. It's a space-charge region during operation and so it is a very narrow region in crystalline silicon. A second question: with crystalline cells and modules we find the fill factor is very fickle and can be affected by many things, both in series and parallel effects, and you have to be very careful if you blame it on a fundamental mechanism, because it may just be a non-uniformity effect in the single cell or series cell.

WRONSKI: I agree 100%. This is one of the results that seems to tie in with the collection efficiency measurements, except that the fill factor follows the contour of an increased field and lower recombination. But of course the fill factor depends on the most parameters, cell material and so on, and unfortunately it appears to be the one that really degrades the most in high-efficiency cells.
ROSS: One of the issues that we asked you about and I'll ask you again -- this is one that is always difficult for us that are researching mechanisms other than the light-induced effect, which is in fact where our primary focus is at JPL. How does one eliminate this effect in terms of measurements that we are trying to make of some of these other irreversible types of degradation mechanisms? Is there something that one can do to sort out that degradation that's associated with light-induced as opposed to -- or inhibited, for example, by applying reverse bias during, say, the accelerated testing of a different type of test?

WRONSKI: That's perfect. Two questions here. One of course, I think, in principle -- although again I think you should talk to the people who are manufacturing modules. If this is a bulk effect it is perfectly reversible. So, therefore, if you don't degrade something else by heating, in principle, you could remove the effect in the bulk. The other thing you asked?

ROSS: Can you inhibit it?

WRONSKI: Of course; that, by the way, has been done. Again relating back to recombination: If you reverse-bias the cell you put a large field, you decrease the recombination, and indeed, people find that the cell does not degrade from the bulk effect. Conversely, by putting it under load you really increase the recombination. So definitely a bias is an important parameter and is one way of differentiating between them.

HERWIG: I hear that CVD potentially does not introduce the problem while glow discharge does. Do you put any stock in that?

WRONSKI: I believe everything the first time I hear it. I have read it more than once. I think it is an open question. Obviously, if you believe that it is structural, that the defects are related structurally, I believe it. I also believe in impurities. I think they are both there but then of course the way you deposit the material is going to be very important. And CVD, in principle, is more gentle. The Japanese are pushing for CVD in a big way. And there, by the way, they are doing it at the junction now rather than the whole film, to reduce recombination of the hetero contact.

TURNER: I'll try and ask this question so that it's illuminating rather than confusing. I'm not sure I know the answer, but I think I do. You made a remark about recombination causing the degradation or by an increase of these things that Xerox calls D states. I hate to use the word instability because I don't think that something that is reversible can be called an instability. You then made the remark that thin devices degrade less than thick devices because the recombination is less. My understanding of this, and I would like to try it out on you, is that when you see degradation, you generally have put the device out in the sun for some hours, or a bright light for some hours, under open-circuit conditions. Under
those conditions, basically, since the absorption in a thin device is very similar to the absorption in a thick device -- to first order, approximately the same -- under open-circuit conditions, then, the recombination must be the same. But the device does not degrade as much because, being a thinner device, it has a higher electric field. So the fact that there are more D states doesn't hurt you as bad. Did I get that right?

WRONSKI: Yes. That's right. The degradation -- you have got the same built-in potential, so therefore the voltage you are putting on it when you operate it is the same in both cases. Now let's look at it in terms of space charge; if you increase the space charge by the same amount in both cells, the field at the other end is going to be much smaller in the thicker cell than in the thin cell, even though you have increased the space charge density by the same amount. That is the way I look at it. Now the other point I would like to ask you is how critical is the operating condition of the cell in the life test, whether you put it under load or whether you put it under under short-circuit current or under open-circuit voltage? Is that a very important factor?

TURNER: It certainly degrades less rapidly if you operate it at the operating point than if you operate it at open circuit. But what the ultimate end point is, I don't know.

HERWIG: Then there is the question of n-i-p vs p-i-n?

WRONSKI: Well, why the differences occur is again because of the way the cell operates. With the n-i-p you are illuminating at the lowest field region, if you assume that the biggest field region occurs at the peak p-i-n site. I would like to say I don't really use the n-i-p much. The primary manufacturers are using p-i-n.