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P. Stradins and H. M. Branz
National Renewable Energy Laboratory

J. Whitaker, J. Viner, and P.C. Taylor
University of Utah

E. Johnson, N. Kherani, and S. Zukotynski
University of Toronto

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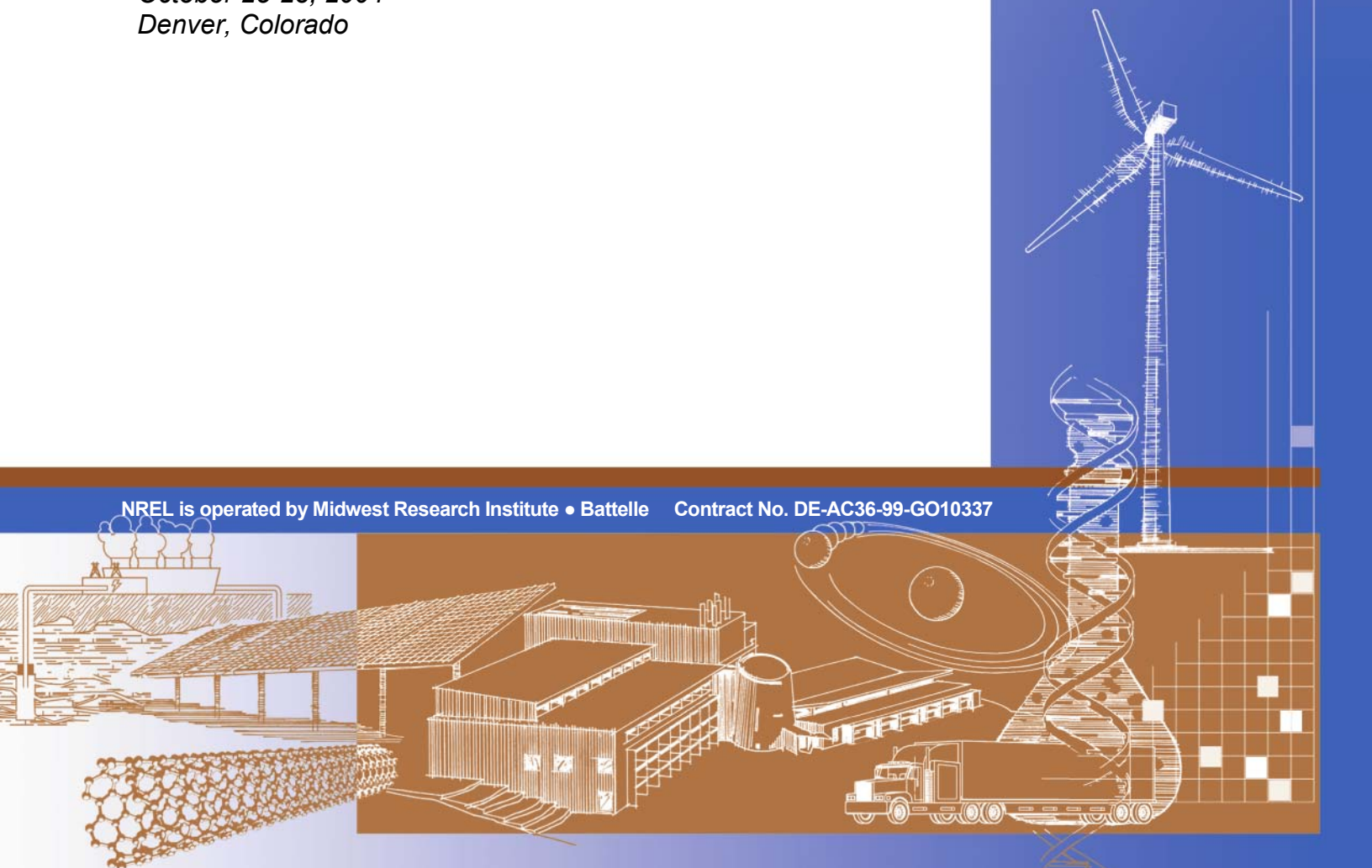

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Tritiated Amorphous Silicon: Insights into the Staebler-Wronski Mechanism

P. Stradins,[a] J. Whitaker,[b] J. Viner,[b] E. Johnson,[c] N. Kherani,[c] H. M. Branz,[a] S. Zukotynski,[c] and P.C. Taylor[b]
[a]National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, pstradin@nrel.gov
[b]University of Utah, Salt Lake City, Utah
[c]University of Toronto, Toronto, Ontario, Canada

ABSTRACT

Hydrogen, though essential for device-quality amorphous silicon, likely contributes to the light-induced degradation process (Staebler-Wronski effect) that reduces the solar cell efficiency by about 4 absolute percent. We are testing the role of hydrogen by using its isotope tritium. When tritium bonded to Si spontaneously decays into inert helium-3, it should leave behind the Si dangling bond defect. We have studied degradation due to tritium and note its resemblance to the Staebler-Wronski effect. Surprisingly, 100x fewer defects are created than expected from the tritium decay rate, suggesting a mechanism that heals most of the defects, even at temperatures down to 4 K. We consider different mechanisms for the thermal and athermal healing processes (e.g. motion of hydrogen, effect of beta-electrons, decay of hydrogen-tritium molecules). Our findings shed new light on the degradation mechanism in a-Si:H and help reveal the role of hydrogen and structural rearrangements near a newly created defect.

1. Objectives

Light-induced degradation of amorphous hydrogenated silicon (a-Si:H) [1] is one of the major factors limiting the performance of thin-film amorphous silicon photovoltaics. Despite 27 years of research, the exact degradation mechanism is still unknown. New approaches to understanding the mechanism are necessary for further progress in a-Si:H cell technology. One of the major problems is to decouple electronic effects (photocarrier generation and recombination) from structural effects (defect creation, hydrogen movement). This is achieved by using the beta-conversion of tritium atoms instead of light excitation. Tritium previously bound to Si beta-converts into inert 3He, leaving behind a Si dangling bond, the same defect observed in light-induced degradation. Thus, a built-in source of defects with a precisely known defect creation rate allows us to study defect creation and annealing in pure form. This will eventually lead to a better understanding of the mechanism of light-induced degradation in a-Si:H and related devices to improve their performance, thus contributing to the *Solar Program Multi-Year Technical Plan.*

2. Technical Approach

a-Si:H films with a fraction of hydrogen replaced by tritium were grown in June 1996 by the University of Toronto group [2]. The samples were made using tritium gas provided by a nuclear power plant, and mixed with silane. They were deposited using a DC glow discharge at substrate temperatures of 150 , 225 , and 250 °C on Corning 7059 glass and silicon substrates. Shortly after deposition, tritium effusion experiments measured a tritium concentration of between 7 and 10 at.%. When we obtained the samples, they were placed in quartz ampoules. Electron spin resonance (ESR) spectra were taken using a Bruker EMX spectrometer at 300 K. The samples were then annealed stepwise for 30 minutes at each temperature in an N_2 environment, and their ESR spectra were taken after each annealing step. After the final annealing step, the accumulation of defects due to tritium decay were monitored by ESR and photothermal deflection spectroscopy (PDS).

ESR measurements were performed at 300 K at microwave power low enough to easily avoid saturating the signal. All ESR measurements were performed at 9.5 GHz with 0.4 mT modulation amplitude at room temperature. ESR measures only paramagnetic centers, i.e. neutral silicon dangling bonds. Because an unknown fraction of the Si dangling bonds might be charged, we performed parallel defect density measurements by PDS.

3. Results and Accomplishments

The first major result of these studies is the following: Si dangling bond defect densities are 3-4 orders of magnitude less than the densities of decayed tritium. Table 1 shows that in all three samples studied, with tritium concentration of 7-10at. % in the as-deposited state, the ESR defect spin densities N_d were below $10^{18}cm^{-3}$ in the as-received state (7 years after deposition, kept at room temperature). At the same time, tritium's beta conversion with a half-life of 12.5 years would produce on the order of 10^{21} cm^{-3} defects. Therefore, there is an ongoing defect annealing process that effectively eliminates 99.9% defects at room temperature.

Table 1. Summary of the sample characteristics and their defect densities in different states.

Sample #	T_{dep} (C)	^3H at.%	N_d as received (cm^{-3})	N_d annealed (cm^{-3})	N_d saturated (cm^{-3})
G181	150	10.4	$5x10^{17}$	$3x10^{16}$	$4.5x10^{17}$
G83	225	7	$4x10^{17}$	$9x10^{16}$	$3.8x10^{17}$
G3	250	7	$1.6x10^{18}$	$3x10^{17}$	$1.4x10^{18}$

As-received samples were then annealed in N_2 atmosphere to 150 °C (G181) and to 180 °C (G83,G3).

The defect densities were reduced by about an order of magnitude (see Table 1). This observation tells us that the annealing of these defects is not a direct reversal of their their creation process, as suggested in a hydrogen model of light-induced degradation [2]. Indeed, tritium converts to an inert ^{3}He atom, which is not involved in any further chemical reactions. Thus, annealing of the tritium-related defects is likely related to the remaining hydrogen (including non-decayed tritium). In such a process, hydrogen attaches to a Si dangling bond without creating a new defect at the location where it was previously bonded. Such H bonding configurations might involve hydrogens forming a two H-complex, or possibly hydrogens on the inner surface of microvoids.

After annealing, the Si dangling bond density increases again and saturates close to the as-received state values within a few months, as seen from Table 1. The time dependencies of this increase were studied in more detail. Indeed, they are interesting to compare with the well-known, yet largely unexplained, $N_d \sim t^{1/3}$ kinetics of defect accumulation under visible light exposure.

The kinetics of the defect spin accumulation in sample G181 at room temperature after annealing is shown in Fig. 1 (solid circles) on a logarithmic time scale. One notices that the increase in defect spin density is much slower than a linear dependence and in fact even resembles $\sim t^{1/3}$ over 3 orders of magnitude in time, from 1 to 300 h. Above 300 h, the defect spin density saturates, approaching the value of the as-received state (shown by a data point at 7×10^4 h).

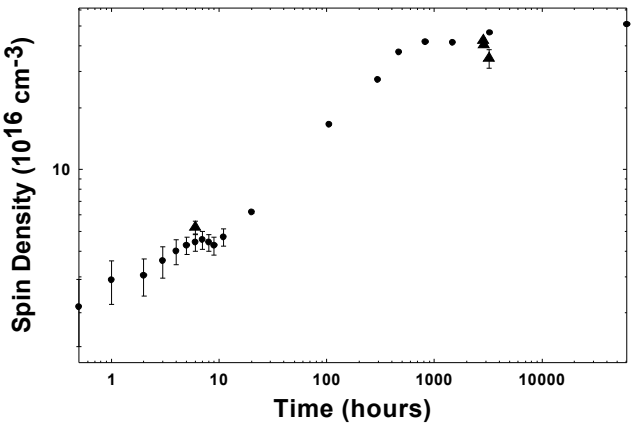

Fig. 1. Accumulation of the defect spins at room temperature in sample G181 after annealing to 150^o C.

To exclude the possibility that the observed low values of defect density N_d and its kinetics do not originate from the defect charging effects, several data points were re-measured using PDS. Unlike ESR, this method is sensitive to all defects, including positively and negatively charged dangling bonds. On Fig.1, PDS data points, shown by solid triangles, are very close to ESR data. This suggests that most of the defects created are neutral, and their low densities and saturation at t > 300 h are not related to charging effects.

Thus, defect creation is accompanied by another very effective process that eliminates most of the defects at room temperature. This eventually leads to their saturation despite an almost constant tritium conversion rate on the order of 10^{16} cm^{-3}/h. Ongoing experiments show that the defect accumulation kinetics at the growth stage is not considerably affected by the temperature, whereas the saturation value is greatly reduced at elevated temperatures. For example, at 80 ^{o}C the saturated N_d value in sample G181 is 6x lower than at 20 ^{o}C and the saturated state is already reached in 20 h instead of 300 h. On the other hand, keeping the sample at 78 K (liquid N_2) leads to a similar, somewhat lower accumulation rate than at 20 ^{o}C, but without showing signs of saturation even after several months. After about 1000 h, the spin density in the sample G181 kept at 78 K is about 10^{18} cm^{-3}, about 2x higher than the saturated value at room temperature.

These new results suggest that the annealing process that reduces the defect density from the number of decayed tritium atoms has both thermal and athermal components that can dominate at different conditions. Emitted 5 keV beta particles may play some role in the athermal component. Establishing the physical mechanisms for these components and their relation to the light-induced degradation is the goal of the future work.

4. Conclusions

Si dangling bond defect accumulation and saturation in a-Si:H due to a built-in defect creation source – a beta-conversion of tritium – reveals that: 1) defects accumulate 3-4 orders slower than defects produced by tritium decay; 2) they follow kinetics that are quite different from tritium decay; and 3) this suggests an effective annealing mechanism, with both thermal and athermal components, which eliminates most of the newly created defects. These findings provide a new angle of approaching solution of the light-induced degradation in a-Si:H solar cells, a key problem for the development of thin-film photovoltaics.

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