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EFFECTS OF BUFFER LAYERS ON SSI CIGSS-ABSORBER TRANSIENT I-V AND C-V BEHAVIOR

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ABSTRACT

Many thin-film CIS photovoltaic devices exhibit a modest level of reversible transient behavior in electrical properties. This paper evaluates this behavior by comparing three cell configurations processed differently. The configurations include CIGSS cells made by Siemens Solar Industries (SSI), SSI absorbers plus buffers/windows done elsewhere, and standard NREL CIGS cells. The buffers used include combinations of the following: KCN solution etching treatment, annealing of the samples after CdS deposition, and/or chemical vapor deposition of ZnO without CdS deposition. All cells made with SSI absorbers showed transient behavior in fill factor, while the NREL cells did not. Post-annealing of devices was found to improve baseline performance and reduce transient behavior.

INTRODUCTION

The modest transient behavior exhibited by many thin-film CIS photovoltaic devices generally improves performance under operating conditions [1]. This modest transient behavior is not an instability, since it is reversible and long-term outdoor stability has been demonstrated for devices that exhibit the behavior. Nonetheless, the changes are a complicating factor when trying to measure or certify the photovoltaic parameters of devices or modules [2], and they have been a designated area of interest to the National CIS R&D Team. While transient behavior has been observed for some time, its cause has not been understood. Hence, in this paper we attempt to better document the effect and identify the root cause of this transient behavior by making modifications to subsequent processing steps for the SSI $Cu(In,Ga)(Se,S)_2$ [CIGSS] absorber. The goal is to correlate transient behavior with the type of absorber and the specific processing steps used to complete the cell.

EXPERIMENTAL

Sample description

In the current study, the subsequent processing steps of the nominally identical SSI CIGSS absorbers include combinations of the following: potassium cyanide (KCN) solution etching treatment, annealing of the samples near 200 °C after CdS deposition (post-anneal), and/or chemical vapor deposition of ZnO without CdS deposition. Resulting cells studied had efficiencies in the 12 - 15% range. The cells without CdS were completed at Washington State University, and they showed somewhat lower (~11%), but still respectable efficiencies [3]. Cells completed using these processes (hybrid cells), as well as cells from prior SSI transient studies, and control cells consisting solely of NREL processing steps, are compared both in their as-manufactured state and after extended light and dark cycles at elevated temperatures. The hybrid CIGSS/CdS cells were made in two separate sets made several months apart with slightly different thickness of their i-ZnO layers.

Transient behavior and cycle description

The details of transient behavior are dependent on the temperature-illumination history of the cell. Conditions studied include dark heat and moderate temperature light soaking. Each soaking cycle is typically 20 hours in duration, though longer times are sometimes needed for complete reversibility. All cells reported in this paper, unless otherwise noted, were subject to 20-hour soaking cycles. During (dark) heat soaking, the cells are in an air atmosphere of 85 °C at zero bias. During light soaking, the cells are near 50 °C at open-circuit voltage under approximately 0.7 suns illumination.

In addition to transient behavior in fill factor and open-circuit voltage determined by illuminated current-voltage (I-V) measurements, changes in the carrier density profiles determined through dark capacitance-voltage (C-V) measurements are observed. The carrier densities and fill factors tend to decrease, and the junction widths tend to increase during dark soaking, but move in the opposite direction with light soaking.

RESULTS

As-manufactured characterization

Significant differences exist among the devices as manufactured. Current density vs. voltage curves are shown in Fig. 1 for a cell etched and post-annealed and a cell not etched or annealed. These cells from the first set of hybrid cells (SSI absorber, completed elsewhere) are representative of the majority of cells prepared by each technique. It is apparent from these plots that the cell etched and annealed is superior. The difference in short-circuit current density is only marginally beyond experimental uncertainty. Although the open-circuit voltage difference is more significant than the difference in current, the 15 mV difference is considered to be quite small.

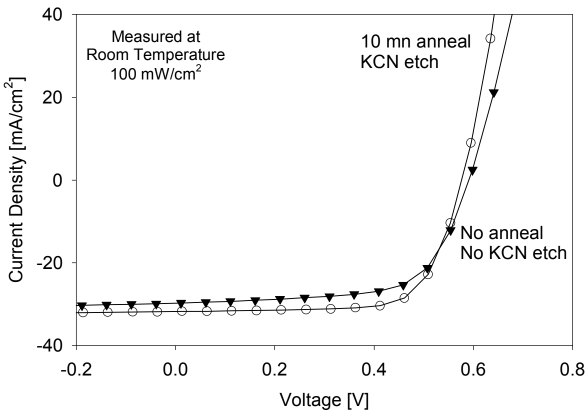

Fig. 1. Current density vs. voltage plots for one etched and annealed cell and one not etched or annealed. SSI absorbers; NREL buffer and window.

Fill factors for this first set of CIGSS/CdS hybrid cells characterized are shown in Fig. 2. This figure shows that most cells made from absorbers etched in KCN and subsequently post-annealed have significantly better as-manufactured I-V performance than cells not etched or annealed. Note, consistent with the example I-V graph, the cells annealed for 10 minutes in the first set of these hybrid cells tend to have better as-manufactured I-V performance than non-annealed cells, and poorer as-manufactured I-V performance than cells etched in addition to being annealed.

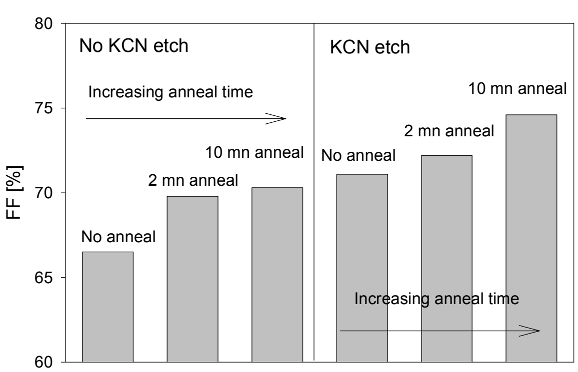

Fig. 2. As-manufactured fill factor as a function of buffer layer for hybrid cells from set one. The bars represent an average of the fill factor for seven cells on one substrate.

A second set of cells was prepared in a manner similar to the first set. However, this time the two minute post-anneal was replaced by a five minute post-anneal, and a slightly thicker i-ZnO layer was used. The fill factors for these samples are displayed in Fig. 3. This second set, where the performance of the etched cells was not always better than that of the non-etched cells, neither supported nor contradicted the benefit of the KCN etch, since the performance difference between the etch/no-etch cells was fairly minimal. The I-V information from both sets, however, clearly shows that the annealing process improves baseline efficiencies, mostly through improvement in fill factor.

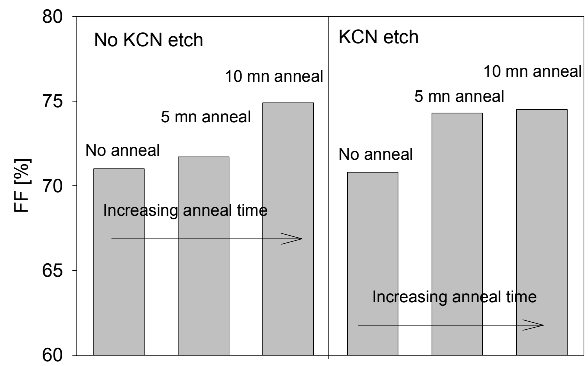

Fig. 3. As-manufactured fill factor as a function of buffer layer for hybrid cells from set two. The bars represent an average of the fill factor for seven cells on one substrate.

In addition to performance differences, the cells also had different carrier-density profiles, as derived from C-V measurements. As seen in Fig. 4, the cells made from absorbers etched in KCN and subsequently post-annealed have a lower carrier density and wider depletion width than cells not etched or annealed. Other measurement results, also included in Fig. 4, have shown that even when the absorbers are not etched, the cells subjected to a 10 minute post-anneal have a lower carrier density and wider depletion width than cells not annealed. The lower carrier density is suggestive of partial compensation of p-type material by n-type dopants. This n-type dopant is likely Cd [4], which presumably diffuses faster at elevated temperature and with the less contaminated surfaces following the KCN etch.

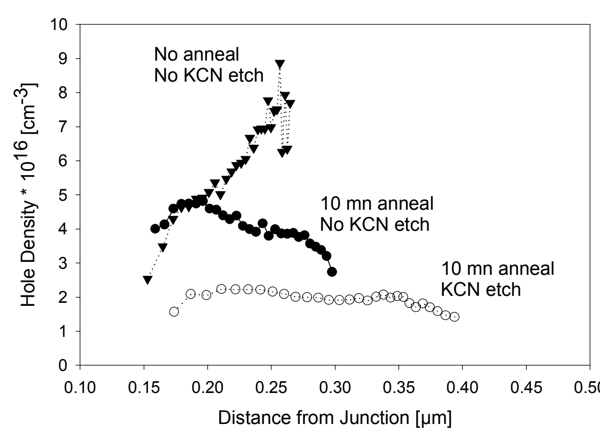

Fig. 4. As-manufactured hole density for hybrid cells from set one.

Transient studies

A typical set of illuminated I-V plots taken after successive dark and light soaks is shown in Fig. 5. The changes are primarily in fill factor; the open-circuit voltage and short-circuit current density remain relatively stable. (The curve with lower photocurrent is likely a calibration issue.) Note also that the plots strongly suggest series resistance as the main cause of changes in fill factor, though closer examination reveals that the first-quadrant data has a small negative curvature.

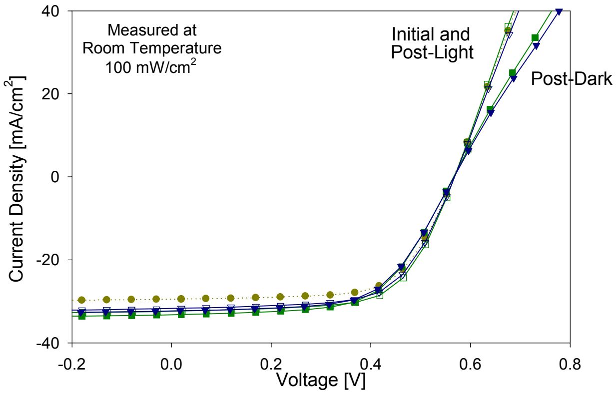

Fig. 5. Illuminated current density vs. voltage graph after each stage of light and dark soaking. This cell was not etched or annealed.

While post-annealing improves as-manufactured performance (Figs. 1 and 2), it merely reduces, but does not eliminate transient effects, as seen in Fig. 6. The cell shown in Fig. 6 was etched prior to CdS deposition and annealed for 10 minutes after CdS deposition.

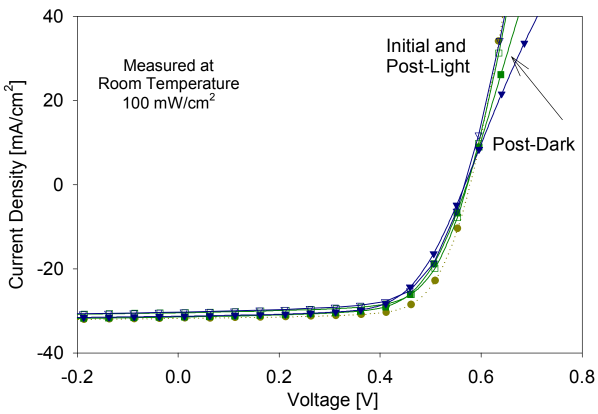

Fig. 6. Illuminated current density vs. voltage graph after each stage of light and dark soaking. The cell was etched and post-annealed for 10 minutes.

The trends in Figures 5 and 6 of varying fill factor, but relatively stable open-circuit voltage and short-circuit current density, are representative of all of the hybrid cells taken through the light and dark cycles. They strongly suggest the increase in apparent series resistance during dark soaking as the main cause of fill factor reduction. This inverse relationship between fill factor and series resistance is evident in all of the cells in this study that were taken through multiple light and dark cycles, including the hybrid cells without CdS. This relationship is elucidated in Fig. 7, which is a compilation of the parameters extracted from light I-V measurements for most of the cell types in this study. For comparison, a cell made entirely at SSI approximately two years ago is included. This earlier SSI cell was subjected to 22-hour cycles with a dark heat temperature of 100 °C and a light soaking temperature of 45 °C.

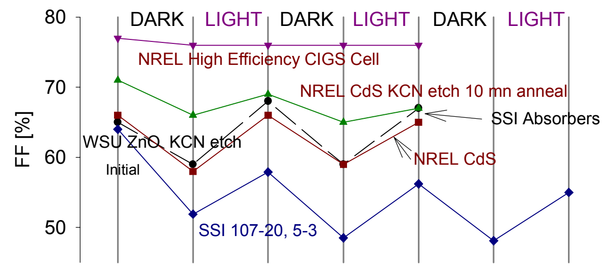

Fig. 7a. Fill factor vs. cycle stage

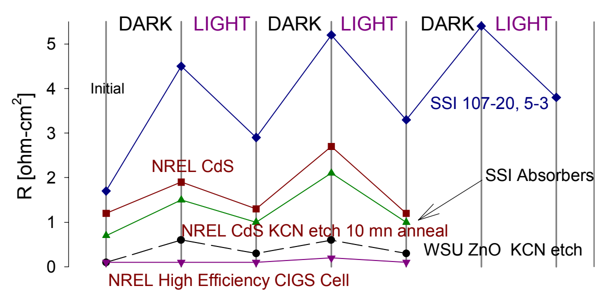

Fig. 7b. Series resistance vs. cycle stage

Note that the NREL high efficiency CIGS cell shows very little transient effect in fill factor. It did, however, show a small transient in open-circuit voltage. It also showed reproducible transient behavior in C-V measurements. The hole densities for the NREL cell changed in a manner similar to what is shown in Fig. 8 for a hybrid cell. Typically the changes were detected a few

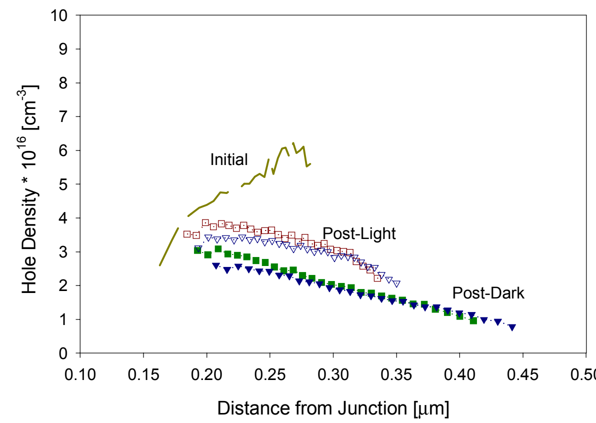

Fig. 8. Carrier-density profile for a cell not etched or annealed.

tenths of a micron into the material. In this and other cells, the hole density change in the first dark heating does not completely reverse, as the initial C-V curve is often not reproduced by subsequent cycles.

The cell shown in Fig. 8 had neither KCN etching nor post-annealing. The transient behavior in the carrier-density profiles derived from C-V measurements is clear. The carrier densities shown in Fig. 8 decrease, and the junction widths increase during dark soaking, and move in the opposite direction with light soaking. Figure 9 shows that this trend is consistent with the majority of the cells taken through the light and dark cycles in this study. Note that this trend is somewhat reduced for the cells etched in KCN compared to the hybrid cell not etched.

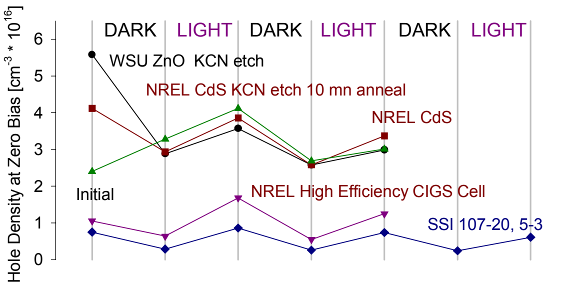

Fig. 9. Hole density at zero bias vs. cycle stage. Fig. 8 cell is labeled "NREL CdS."

The compilation of above figures suggests that although the hole density and the fill factor change in the same direction with light and dark soaking, one does not actually cause the other. For example, the as-manufactured results show that the cells with the best fill factors also have the lowest hole densities (see Figs. 3 and 4). Figures 7a and 9 serve to further confirm that higher hole density does not require higher fill factor, as the same cell that has an increasing hole density (NREL CdS KCN etch 10 mn anneal) from initial conditions through the first light soak shows a transient fill factor through this same set of dark and light soaks. Thus, while the same mechanism may be causing the fill factor and hole density changes during the cycling, a higher hole density is not enough to assure better performance overall. This is qualitatively consistent with modeling work done by Hong Zhu and others [5].

DISCUSSION AND RECOMMENDATIONS

This set of experiments has shown that the nature of the transient effect is primarily dependent on the source of the absorber material. It has also supplemented previous observation of the reversibility through illumination of the effects brought about by the dark heat. Additionally, this set of experiments has shown that post-annealing can be beneficial not only in improving baseline performance, but also in reducing transient effects. Although changes in hole density and fill factor are correlated during transient cycles, the former is not the likely cause of the latter. However, both may well be the result of the same mechanism.

All the cells made with Siemens absorbers show qualitatively similar transient effects that are not seen in the NREL-absorber cells. Furthermore, the carrier-density profiles derived from capacitance show that changes occur within a few tenths of a micron of the junction. The fact that the I-V curves are modified by light soaking strongly implies that the changes occur in the spatial region where photons are absorbed. Two possible mechanisms are suggested: a significant density of long-lived traps in the part of the absorber close to the junction, or the actual movement of atoms. One problem with the measurements to date is that both illumination and bias were different in the light and dark cycles. Thus one recommendation is to maintain the same bias during the soaking cycles to separate these possibilities. A second recommendation is to do the light soaking separately for photon energies above and below the window (generally CdS) bandgap. A third recommendation suggested by the forward-current negative curvature is to extend the analysis range to higher currents and reduce the temperature slightly to give a clearer picture of possible current-limiting effects.

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