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Sourabh Dongaonkar
Purdue University - Main Campus, sourabh@purdue.edu

Erik Sheets
Purdue University

Rakesh Agrawal
Purdue

Muhammad A. Alam
Purdue University - Main Campus

Reverse Stress Metastability of Shunt Current in CIGS Solar Cells

Sourabh Dongaonkar[1], Erik Sheets[2], Rakesh Agrawal[2], and Muhammad A Alam[1]

[1]School of Electrical and Computer Engineering, Purdue University, West Lafayette, USA
[2]School of Chemical Engineering, Purdue University, West Lafayette, USA

Abstract — **Partial shading in thin film solar panels can result in reverse bias stress across shaded cells. Therefore, it is important to understand the effect of such reverse stress in commercially competitive PV technologies such as CIGS. In this paper, we systematically investigate the effect of moderate reverse bias on solution-processed CIGS solar cells. We subject the solar cells to varying degrees of reverse biases and continuously monitor the impact of the stress on dark current. We also explore the relaxation behavior of dark current following passive storage and the long term effect of the shadow stress on power output of the cell. We find that the reverse stress affects only the localized shunt current paths, without affecting the bulk device characteristics. The shunt current exhibits a metastable change with reverse stress, and can increase or decrease on application of reverse stress. We analyze this phenomenon in detail, and discuss the hypothesis that can explain its characteristic features.**

Index Terms — **semiconductor device breakdown, photovoltaic cells, shunt, CIGS.**

I. Introduction

$Cu(In,Ga)Se_2$ or CIGS solar cells have attracted great attention, due to their high efficiencies, and adaptability to low temperature, large area manufacturing process [1], [2]. Several manufacturing challenges must be addressed [3], however, before CIGS technology can become a viable competitor to conventional c-Si based photovoltaic on industrial scale. Specifically, these include variability and reliability issues, which govern panel yield, and long term field performance, respectively [4]. One such key reliability concern is the partial shading of panels, because in a series connection of cells inside a panel, partial shading can cause reverse biases across shaded cells [5]. Given its importance, the phenomenon has been studied extensively in c-Si cells [6], but for thin-film solar cells the problem remains less well understood.

Previous thin film PV research has shown that partial shading predominantly causes moderate reverse voltages across shaded cells [7] that could cause long term performance degradation in the panel. Understanding the implication of such reverse stress is therefore critical for estimating panel performance over time in realistic operating conditions. Unlike previous studies [8], however, we focus on the stress behavior of individual cells, and restrict ourselves to moderate reverse biases. Prior a-Si:H research has demonstrated that these moderate reverse stresses have very different impacts on the diode [7] and shunt current degradation [9].

In order to understand the physical mechanism of such reverse stress induced degradation in other technologies, a similar distinction between diode and shunt degradation is necessary. These stress tests also offer deeper insights into the formation and impact of parasitic shunt current paths in these cells. This can help in reducing the effect of parasitic losses at the panel level, thus reducing the gap between cell and panel efficiencies. In this paper, we report a systematic characterization of the dark and light characteristics of solution processed CIGS solar cells, before and after reverse stress, and identify the major degradation features.

II. Cell Fabrication

To synthesize CIGS nanocrystals, a room temperature solution of sulfur and oleylamine was hot-injected into a solution containing copper-, indium-, and gallium-acetylacetonates in oleylamine under a nitrogen atmosphere at 285°C. After reacting for 30 minutes, $Cu(In_{0.7},Ga_{0.3})S_2$ nanocrystals were isolated and washed with hexane, methanol, and isopropyl alcohol before dispersing in hexanethiol to form an ink. Thin films were cast by doctor blade technique on a 2x1 inch piece of molybdenum coated soda-lime glass and etched with potassium cyanide for removal of detrimental sulfide binaries. After dipping in a NaCl and water solution, the films were cut into two 1x1 inch squares and annealed in a selenium vapor environment forming $Cu(In_{0.7},Ga_{0.3})(S_{1-y},Se_y)_2$, as described by Guo et al. [10]. A thin buffer layer of CdS was applied by the reaction of cadmium sulfate and ammonium hydroxide with thiourea in a chemical bath deposition process. ZnO and tin doped indium oxide were respectively sputtered on the surface, and Ni/Al grids completed the device. Each 1x1 inch square substrate contains 6 cells which were characterized independently.

III. Stress Measurements

We subjected 18 similarly processed cells to a 3 step measure-stress-measure cycle, with increasing reverse stress. The stress involved a reverse voltage sweep with increasing magnitude of -2V, -3V to -4V. Each stress sweep was preceded and followed by a measurement step, in which the dark current (I_{Dark}) was measured from -1V to 1V. Finally, the samples were allowed to relax in dark (without stress) for several weeks, and the dark and light IV were measured again to check if the observed effects of stress are permanent. We find that characteristics of some cells revert to press-stress values. In order to identify the physical origin of this

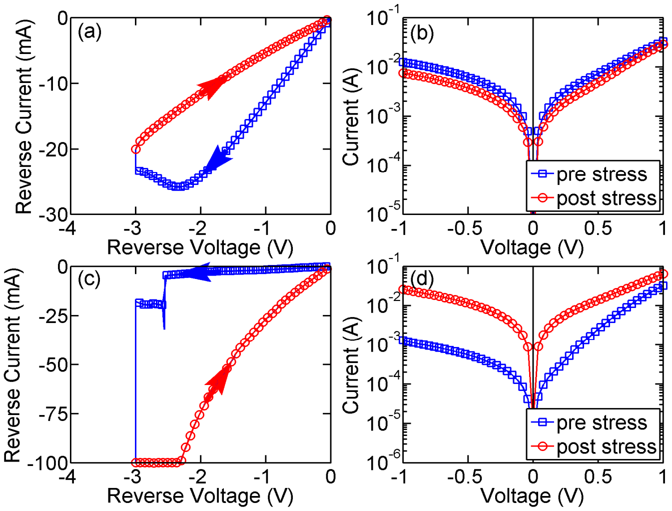

Fig. 1. (a) Reverse current hysteresis for 0 to -3V sweep, showing reduction in current with stress (arrows show direction). (b) Dark IV before (blue squares) and immediately after (red circles) stress shows similar decrease. (c) Similar reverse sweep to -3V in other cell, results in abrupt increase in current, limited by compliance. (d) Comparison of dark IV also mirrors the corresponding increase in current.

relaxation, we have analyzed the time-dependent relaxation kinetics of these samples, as discussed below.

A. Switching transitions in dark current

We observe that on application of reverse bias, the dark current shows pronounced hysteresis, and the current changes by a factor of 2-3 as the bias is swept from 0 to -3V, see Fig. 1a. The effect of this reverse-stress is also reflected in the low-voltage dark IV measured immediately before and after the stress, as shown in Fig. 1b. Similar hysteretic transition has been observed for a-Si:H cells [11], and is qualitatively analogous to the OFF transitions observed in non-volatile resistive switching memories (ReRAM) [12].

On the other hand, some cells show an abrupt increase in reverse current on application of reverse bias. As shown in Fig. 1c, the current jumps by about an order of magnitude during similar 0 to -3V sweep, analogous to ON transitions in ReRAM. This change is also reflected in the low-voltage dark IV curves before and after the stress, which are compared in Fig. 1d. We note that OFF transitions, where reverse current decreases are qualitatively similar for all samples, however, these OFF transitions are less abrupt compared to ON transition. Similarly, the ON transitions, where the increase in I_{Dark} is very abrupt are also qualitatively consistent across different samples. This suggests that different physical processes are probably driving these transitions.

B. Features of switching behavior

We find that of the 18 cells measured, 4 cells showed only OFF transition resulting in reduction in I_{Dark}; another 4 showed only ON transition causing an increase in dark current, and 2 cells initially showed an OFF transition, followed by an ON transition at higher stress. For the remaining 8 cells, no change in the dark IV was observed because of reverse stress.

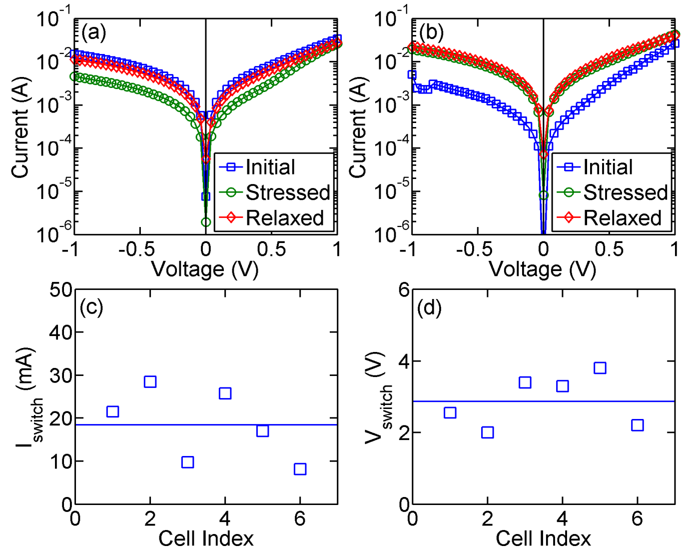

Fig. 2. (a) Initial dark current (blue squares), which reduces after OFF transition (green circles), then relaxes back to original value (red diamonds). (b) In case of ON transition, the change is permanent. (c) Threshold current for OFF transition for all 6 cells is close to 20mA. (d) The ON transition is voltage triggered, with a threshold voltage of about 3V reverse bias.

The ON and OFF transitions of all cells exhibit certain common features which can help us understand their physical origins. The first of these features is the relaxation of dark IV. For all cells showing the OFF transition due to stress, we find that the dark current is restored to its original value after passive storage in dark for several weeks (Fig. 2a). In contrast, the increase in dark IV after ON transition, appears to be permanent and shows no change after prolonged storage in dark (Fig. 2b). Moreover, the ON and OFF transitions show distinct current and voltage thresholds for switching. We found that all OFF transitions appear to be triggered at a reverse current threshold of approximately 20 mA (Fig. 2c), while ON transitions are apparently controlled by the magnitude of reverse stress voltage with a threshold of approximately 3 V (Fig. 2d). We note that this metastable behavior is most apparent in low to medium efficiency samples, and therefore, a deeper physical understanding of the problem may lead to processing options to reproducibly fabricate high-efficiency cells.

IV. Discussion

The dark IV of solar cells can be represented as a parallel combination of exponential diode current (I_D) and a symmetric, parasitic shunt current (I_{SH}) [13]. Since the reverse saturation current of a diode is very small, we can approximate I_{SH} as reverse dark current (i.e., $I_{SH} \approx I_D(V < 0)$). And, owing to the universal symmetric non-Ohmic shunt conduction in thin

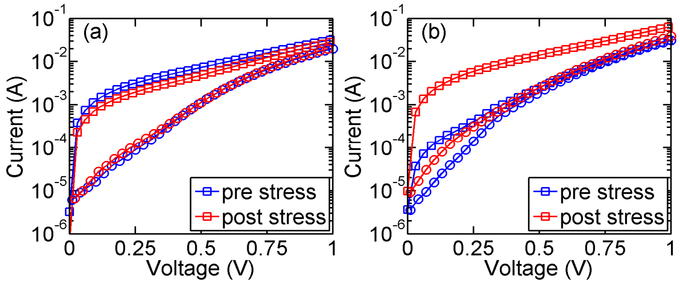

Fig. 3. (a) Measured forward current (squares), before (blue) and after (red) reverse stress, showing the OFF transition. The cleaned forward diode current (circles) however, shows no effect of the reverse stress. (b) Increase in forward IV after ON transition (blue vs. red squares), due to reverse stress. Just like the OFF transition the cleaned I_D shows little impact of reverse stress (blue and red circles).

film cells [14], we can utilize the voltage symmetry of I_{SH}, we can subtract off I_{SH} from forward I_D [15]. This allows us to look at the effect of stress on both current components separately.

A. Metastability in I_{SH}

Fig. 3a shows the OFF transition apparent from measured pre and post stress forward dark current (squares). However, when the shunt current is subtracted off, the forward diode currents overlap each other (circles). This means that the reduction in I_{Dark} due to reverse stress is attributed solely to a reduction in I_{SH}. In case of ON transition too, (Fig. 3b) the subtraction of shunt current results in near overlap of the pre and post stress I_D. The small discrepancy in pre and post stress I_D in Fig. 3b, is due to the limited precision of the measurement apparatus. This subtraction yields similar results for all devices that show ON/OFF switching behavior. Therefore, we can attribute any change in dark current due to reverse stress to an increase or decrease in I_{SH}, with no change in the bulk diode current.

B. Current relaxation kinetics

In order to explore the relaxation behavior after OFF transition, we performed transient measurements by observing the post stress reverse current as a function of time. This was done by observing the reverse current (at -0.1V) over time immediately following the reverse stress sweep (Fig. 4a). Fig. 4b shows the reverse current transient after stress in perspective with the pre and post stress currents. It seems that the relaxation in I_{SH} after stress happens in two stages. The fast transient has a time constant < 0.1 s and recovers about half the change in I_{SH}. The slower transient, which is easily measurable, lasts for about 10^4 s, at the end of which I_{SH} recovers almost completely. These observations regarding the recovery kinetics suggest that the OFF transition is probably a result of charge trapping rather than trap generation because of the low to moderate time constant of recovery [16].

C. Impact on solar cell characteristics

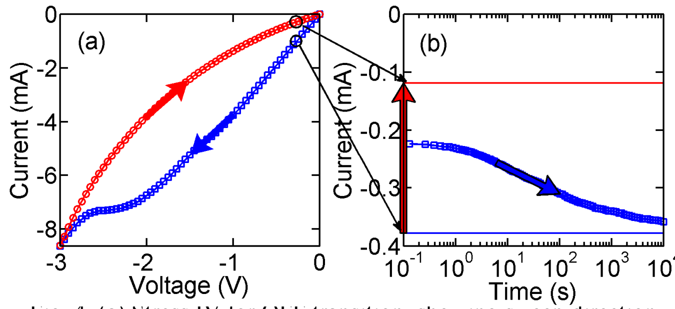

Fig. 4. (a) Stress IV for OFF transition, showing sweep direction, and the transient measurement points (circles). (b) Transient relaxation of shunt current after stress shows a fast transient (< 0.1 s), and a slow transient component (~10^4 s), after which the current saturates close to its pre stress value. Arrows show the direction of change in current with time.

These observations imply that any change in device characteristics with stress is a result of a change in behavior or number of localized shunt paths, and the bulk device behavior is not altered by reverse stress. In order to check this hypothesis, we compare the typical solar cell parameters of all solar cells, before and after the stress-relax measurement cycle. Fig. 5a shows the scatter plot of final vs. initial efficiency of the cells. As expected, the cells with stable shunts show no impact of reverse stress on efficiency. This again affirms that the bulk of the solar cell is not affected by reverse stress. On the other hand, the cells which show large increase in I_{SH} due to reverse stress, show significant drop in efficiency. The fact that this drop is caused solely due to higher shunting is also evident when we compare the other solar cell parameters. Note that the efficiency loss in cells showing ON transition, is mainly due to significant degradation in fill factor (Fig. 5d), and some reduction in open circuit voltage (Fig. 5b), while the short circuit current (Fig. 5c) shows little change. This is also consistent with the claim that increased shunting in post stress cells is responsible for significant efficiency losses. In the remaining 4 cells which had shown some reduction in I_{SH} on stress, but had relaxed to their original value, the trends in efficiency are not conclusive. Although, as seen in Fig. 5, it does seem that some cells show a little improvement due to smaller shunts.

D. Physics of shunt metastability

Based on these measurements, we can try to understand the reasons behind stress behavior of shunts. We found that the reduction in I_{SH} relaxes to its original value with time. Also, these OFF transitions were found to be less abrupt and triggered near a current threshold. These observations suggest that the OFF transition is possibly a result of charge trapping in the existing shunt paths of the solar cells. Shunts in CIGS cells are formed due to localized parasitic Metal-Semiconductor-Metal paths formed during fabrication. This leads to a space charge limited shunt in parallel to the diode current [14]. The traps in these shunt paths can be charged at higher biases resulting in temporary change in characteristics.

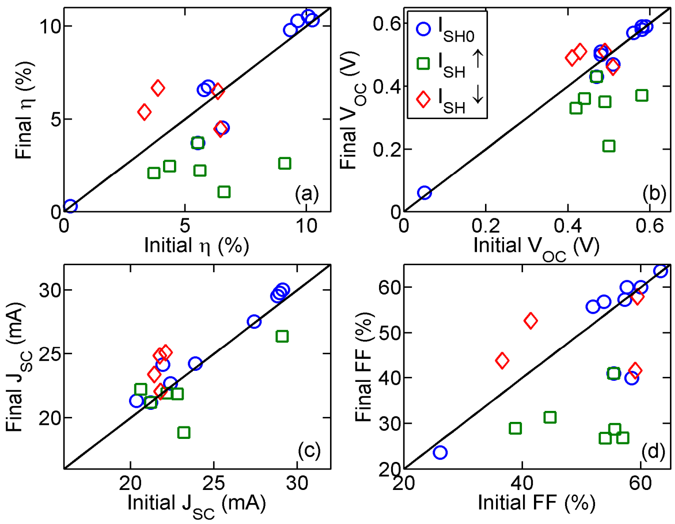

Fig. 5. Scatter plots comparing the initial and final solar cell parameters for the measured cells, namely, (a) efficiency, (b) V_{OC}, (c) J_{SC} and (d) fill factor. The stable cells, where ISH had not changed with stress (blue circles), show little change. The cells where I_{SH} had increased (green squares) show lower efficiency due to lower FF and V_{OC}. And, some cells where I_{SH} had reduced (red diamonds) show marginal improvement.

Further measurements on the relaxation kinetics are underway to understand this transition better.

In contrast, the abrupt increase in I_{SH} triggered by reverse voltage is most likely caused by the formation of a new shunt path. Since the CIGS film surface is never perfectly smooth, the local regions with sharp edges or peaks result in higher local electric fields, especially during reverse stress [17]. Therefore, it is conceivable that during ON transition a local high electric field region experiences a breakdown in the CdS layer [18]. This will result in the formation of a new shunt path, because the junction will be destroyed locally. As this high field breakdown is followed by a large surge of current, there can be permanent damage to the local CdS region, leading to the permanent increase in total I_{SH}. We note that similar mechanism of ON transitions has been reported for metastable shunts in a-Si:H p-i-n solar cells [11]. Owing the similar phenomenology of shunting in both cells, it is likely that similar electric field driven processes are responsible for stress induced new shunt creation in solution processed CIGS cells as well.

VI. Conclusion

We demonstrate that shunt current in solution processed CIGS solar cells exhibits a metastable switching behavior on application of reverse bias. We found that for some cells I_{SH} decreases by a factor of 2-3, due to reverse stress. This change is reversible, and I_{SH} relaxes to its original value upon storage in the dark. On the other hand, I_{SH} can increase by an order of magnitude, due to stress, and this ON transition is more abrupt and permanent. The data suggests that the OFF transition is probably caused by the change in characteristics of individual shunts, and the ON transition is due to a local breakdown in the CdS emitter layer. The trends in switching transitions suggest that even moderate stresses arising from partial shading can cause significant permanent damage in solar cells, and any marginal improvement in other cells will be temporary.

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