Large-Area Material and Junction Damage in c-Si Solar Cells by Potential-Induced Degradation

Preprint

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Presented at the 2018 World Conference on Photovoltaic Energy Conversion (WCPEC-7)
Waikoloa, Hawaii
June 10–15, 2018

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Suggested Citation
Xiao, C., C.-S. Jiang, S.P. Harvey, J. Liu, H. Moutinho, P. Hacke, S. Johnston, and M. Al-Jassim. 2018. "Large Area Material and Junction Damage in c-Si Solar Cells by Potential-Induced Degradation." *Preprint*. Golden, CO: National Renewable Energy Laboratory. NREL/CP-5K00-70819. https://www.nrel.gov/docs/fy19osti/70819.pdf.

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Conference Paper
NREL/CP-5K00-70819
October 2018

Contract No. DE-AC36-08GO28308

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Large-Area Material and Junction Damage in c-Si Solar Cells by Potential-Induced Degradation

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Abstract — **In this work, we discuss a new fundamental PID mechanism that has not been reported. We developed in-situ Kelvin probe force microscopy to monitor the potential evolution at nanometer scale under high-voltage stress. We observed large-area junction degradation during the stressing and junction recovery by heat treatment from the same location. Electron-beam induced current (EBIC) results support the large-area damage, which has a much lower collected current (dark region) and has an abrupt transition between the bright and dark areas, in addition to local shunts. Transmission electron microscopy does not find stacking faults in the dark-EBIC region. Furthermore, time-of-flight secondary-ion mass spectrometry indicates that the large-area damage correlates with more sodium content. The consistent results shed new light on PID mechanisms that are essentially different from the widely reported local-junction shunts.**

Index Terms — Potential-induced degradation, Si, large-area damage, sodium, microscopy.

I. Introduction

Potential-induced degradation (PID) of crystalline Si modules has been an important reliability issue [1]. It has been widely reported that PID is related to sodium ions penetrate into extended defects that penetrate p-n junction, thus causing local electrical shunting [2]–[4]. In this work, we discuss a new fundamental PID mechanism that has not been reported. Sodium (Na), in addition to penetrate into stacking faults, likely penetrate widely into the bulk and causes large-area material and junction degradation by forming point defects. In the 2017 PVSC, we reported a large area of millimeter-scale material and p-n junction damage caused by PID, and the electrical transition is abrupt between good and damaged areas [5]. In this paper, we developed *in-situ* Kelvin probe force microscopy (KPFM) to monitor the potential evolution at nanometer scale under high-voltage stress. We observed junction degradation during the PID stressing and junction recovery by heat treatment from the same location. Electron-beam induced current (EBIC) results support the large-area damage, which has a much lower collected current (dark region) and has an abrupt transition between the bright and dark areas, in addition to local shunts. Transmission electron microscopy (TEM) does not find stacking faults in the dark-EBIC region. Furthermore, time-of-flight secondary-ion mass spectrometry (TOF-SIMS) indicates that the large-area damage correlates with more Na content. The consistent results shed new light on PID mechanisms that are essentially different from the widely reported local-junction shunts.

II. Experiment Details

KPFM is an atomic force microscopy (AFM)-based technique that measures the electrostatic potential on a sample's surface with a 30-nm spatial resolution and a 10-mV potential resolution [6]. We have developed *in-situ* high-voltage stressing capability on an AFM platform and successfully applied KPFM to investigate the PID issue [7]. The KPFM measurements on cross-sections of silicon solar cells allow direct imaging of the evolution of the electrical potential across the p-n junction during the degradation process.

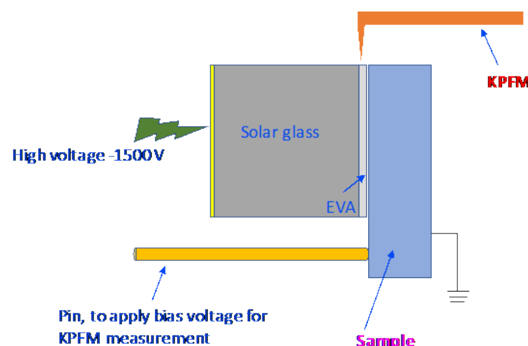

Fig. 1. *In-situ* stressing capability with KPFM measurement

To simulate the PID process, the sample architecture is made to be identical to a real module: a piece of multicrystalline Si cell is covered by pre-polymerized ethylene vinyl acetate (EVA) and a tempered solar glass. The cell studied in this work is the conventional aluminum back-surface-field (Al-BSF) p-type Si cell, with a single front junction formed by a phosphorous-doped emitter and SiN_x on the top surface. Because the KPFM technique requires a flat surface, the cross-sectional sample was chemical-mechanically polished to make the overall cross-section surface corrugation less than 20 nm. Figure 1 shows a schematic of the *in-situ* characterization. A constant bias voltage of -1,500 V was applied to the shorted cell-piece with glass and EVA at a temperature of 25°C for over 40 days. Note that this timeframe is much longer than in regular PID accelerated life testing (~two weeks) [4]. The potential profiles were monitored by KPFM. In the measurement, we applied different small bias voltages across the cell V_b = -1.5 ~ +1 V. The longer stress time is usually necessary in our case. PID may randomly cause highly-nonuniform defective areas even though a uniform high voltage is applied.

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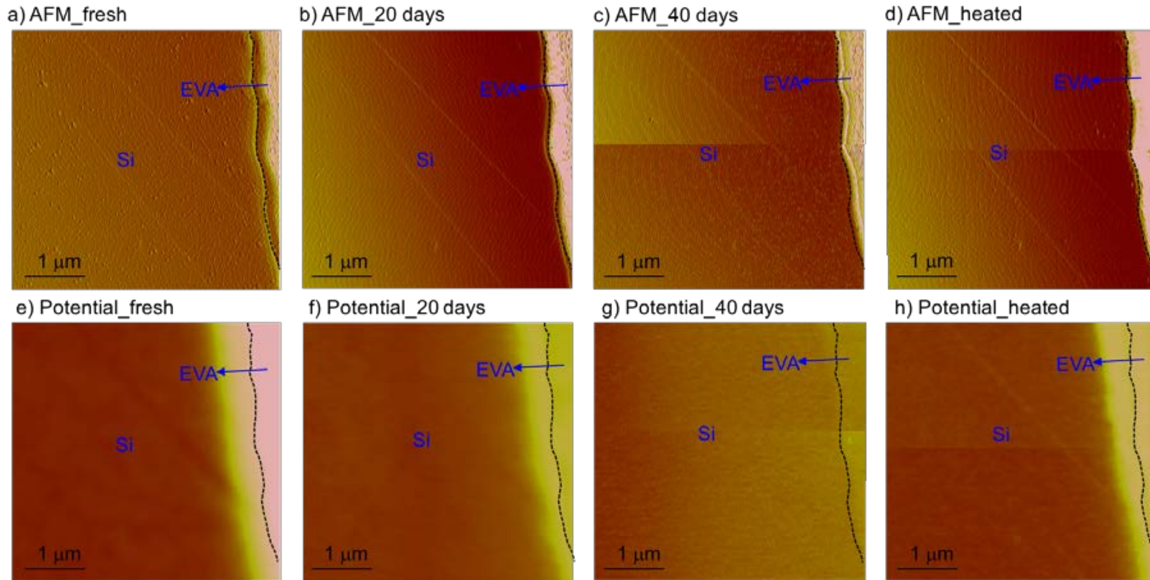

Fig. 2. a)–d) AFM images indicating the same characterized location under stressing and recovery; e)–h) KPFM mapping of potential evolution across the p-n junction for over 40 days, corresponding to a–d.

We cannot control exactly how long time we need to apply the high voltage, to make the area involving the cross-section get significantly degraded. However, we usually observed the degradation after certain stressing time by monitoring the change in the potential image.

In parallel, a sample from the same Si cell went through similar PID stressing and was characterized by dark lock-in thermography (DLIT), EBIC, TEM, and TOF-SIMS. Note that after the laboratory PID stressing, the cell was extracted without mechanical damage to avoid possible measurement artifacts. This is a multiscale approach: 1) DLIT images large scale at hundreds μm to roughly determine the degraded areas; 2) higher-magnification EBIC mapping was done at the same degraded location; 3) TOF-SIMS analyzed the chemical contamination on the same area as EBIC, and 4) TEM investigated the dark EBIC area.

III. Results and Discussion

We used the *in-situ* stressing capability in KPFM measurements and monitored the potential evolution across the p-n junction along with stressing voltage of -1,500 V for over 40 days. We found that the potential evolution is uniform on a long range over hundreds of µm: PID stressing shifts the potential-drop location to the cell front-surface and the potential amplitude decreases gradually to ~0. The potential drop at the junction area eventually smears out. Heat treatment partially recovers the degraded area. The results are shown in Fig. 2. AFM images (Figs. 2a–2d) show that the measurements were taken in the same location. The Si/EVA interface is indicated by the black dashed line. KPFM potential images (Figs. 2e–2h) were taken at reverse-bias voltage of -1.5 V. Initially, a fresh cell is measured in Figs. 2a and 2e. In Fig. 2e, the applied voltage drops the most (the potential change between bright and dark areas) at ~500 nm to the Si/EVA interface, indicating a normal p-n junction. After 20 days of PID stressing, the potential-drop position shifted ~200 nm toward the Si front surface (Fig. 2f). As the stressing continued for 40 days, the potential drop was no longer measured (Fig. 2g), suggesting a full collapse of junction potential. After thermal annealing at 300℃ for 30 min, we observed a junction recovery. However, the recovery is not fully healed back to a normal junction (Fig. 2e), and potential-drop position and amplitude are similar to Fig. 2f, suggesting a partial recovery. Note that Figs. 2c, 2g, 2d, and 2h were combined by two consecutive scans, because we scan a very large area of ~350-µm total length along the junction every time period with every scan of 5×5 µm^2. These results are similar to what we observed in our *ex-situ* KPFM characterization [5].

Another piece of plan-view sample was cut out from the same fresh cell as used in the KPFM imaging. This piece went through PID stressing with -1500 V stressing for 60 days at room temperature (RT). Then, this piece was studied by DLIT and EBIC, with results shown in Fig. 3. Figure 3a is the optical image of the sample, and Fig. 3b is the DLIT phase image taken at -1 V reverse bias, which showed several degraded locations. But due to the relatively low spatial resolution of the technique, we cannot determine whether they are point shunts or large-area degradation. We used EBIC to zoom into the area indicated by the purple rectangle. We could not distinguish a crack at the location of the sharp change of dark and bright regions by SEM (Fig. 3c). However, figure 3d clearly showed a large area of weak current collection (dark region), and the transition between dark and bright region is sharp. Note that in both the dark and bright regions, there are dark points induced by the effect of surface roughness. The EBIC line profile along the orange line in Fig. 3d (blue curve) is overlapped in the image. The large dark region can be caused by poorer qualities of both/either the underlying Si material and/or junction, such

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as shorter minority carrier lifetime (SHR recombination) and larger diode quality factor (junction recombination) than the brighter area. However, it should not be caused by the effect of point shunts nearby, because of the abrupt change of EBIC signal. The abrupt EBIC signal change may be due to different PID accessibility in different orientations of the two grains but should not be due to the original lifetime before PID, because of the higher Na content of the dark EBIC area than the bright area, as shown later. Investigation of grain orientation and structure by TEM is under way.

Further, the EBIC areas were analyzed by TOF-SIMS to investigate the chemical impurity, especially searching for Na^+. Figure. 4a shows the 3D render of Na^+ on the 500 ×500 μm^2; the Na^+ impurity map is correlated to the EBIC dark region. There is significantly more localized Na^+ that has been attributed to Na-decorated extended defects [4] on the lower right region than the upper left region. In Fig. 4b, we take the depth profiles in areas away from the localized highly Na-contaminated area but still in the region with dark EBIC signal. The red and blue points indicate the location for taking the Na^+ profiles. The dark-EBIC region has a Na^+ concentration of mid 10^{19} cm^{-3}, whereas Na is 2–5 times less in the bright-EBIC region. Also, we did TEM on a random area in the dark-EBIC region, and no extended defects were found in this random lift-out region (15 μm long x 100 nm wide ×15 μm deep). We note that this is a small sampling area compared with the EBIC and SIMS imaged area, should not involve a loalized highly-Na decorated region. However, in this area, Na content should approximately be in mid-10^{19}/cm^3 (the red curve in Fig. 4b) and higher than the bright-EBIC area (blue curve).

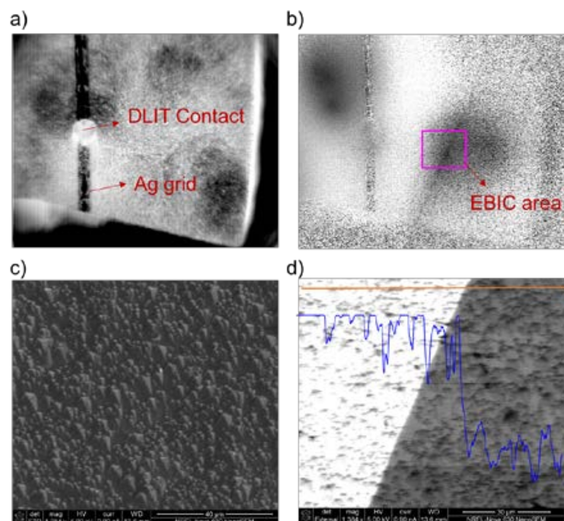

Fig. 3. a) optical image of a stressed Si piece; b) DLIT phase image of the Si corresponding to a); c) SEM image of EBIC area; d) EBIC mapping of the purple rectangle area indicated in b).

Besides the localized regions of high Na concentration going into the depth of the Si, the common heavier Na^+ concentration in the dark-EBIC region suggests a higher

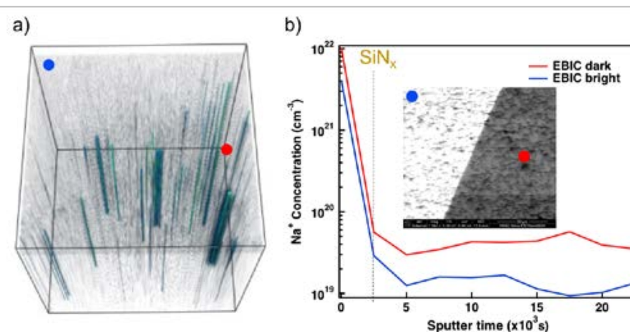

Fig. 4. a) TOF-SIMS 3D render of Na^+; b) Na depth profiles of EBIC dark and bright area; inset is EBIC image, and the red and blue spots indicate the location of Na profiles taken.

concentration of point defects in the heavily PID-degraded

area. Point defects formed by Na^+ in Si have been reported to induce six gap states, two of which can be detrimental for PV, with one at 0.27 eV above the valence band maximum (VBM) (deep level) and the other being donor-like at 88 mV above the VBM [8]. These two defects can degrade the solar cell performance by different mechanisms of Shockley-Read-Hall (SRH) recombination and altering doping around the junction and in the Si bulk. More importantly, Na^+ concentration in the PID area is high, on the order of up to 10^{19}/cm^{-3} (for reference, the average Na^+ concentration in Si bulk in ref. [8] is 10^{13}/cm^{-3}); so this level can cause massive SRH recombination and massive lifetime degradation. If a p-n junction is formed by Si material with such a poor quality, the junction cannot be well formed with very leaky carrier transport through the gap states, causing a large J_0 and small equivalent resistance (R_j) of the junction. KPFM measures the voltage drop by measuring the potential change induced by applying a bias voltage to the device. If R_j is significantly smaller than the series resistance of other parts than the junction (including the electrical contacts and conduction lines), then the voltage drop will not be at the junction and KPFM shows no or a small voltage drop at the junction location. As for the effect on EBIC, if the lifetime of Si material is much degraded by SRH recombination, then minority carriers cannot be collected by the junction before they recombine, making a small EBIC current. On the other hand, the donor-like state is just above the VBM, lower than all other acceptor-like states; so this level with the high Na concentration can largely alter the p-doping of Si on the order of ~10^{16}/cm^{-3}—making the p-n doping boundary and the bulk p-doping nonuniform, and also making the doping of both n and p around the junction much smaller than the original p-n junction, and thus, widening the depletion region. This potential profile is consistent with the poor and irregular p-n interface with much lower carrier concentrations at both the p and n sides. To increase confidence in the analysis, macroscopic regions that show high Na^+ point defects without localized regions of high Na concentration going into the depth of the Si (from 2D or 3D defects) remain to be isolated. Further, models for why Na may penetrate certain grains as point defects and not others, and by what mechanism Na may be introduced into the Si bulk remain to be clarified. On another

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hand, the localized highly Na-decorated extended defects may couple with relatively high-Na content nearby, and both the extended defect and the surrounding area may all contribute to the PID with different mechanisms.

IV. CONCLUSION

We found a new PID mechanism of silicon modules that is different from and complementary to the current knowledge that PID shunts are localized in small and separate spots. We found that degradation not only occurs in stacking faults, but also, can cause materials and junction damage across large areas. *In-situ* KPFM results showed uniform potential evolution across the p-n junction; DLIT, EBIC, and TEM results are consistent with the large-area degradation. And TOF-SIMS indicated that Na is also correlated to the PID in a large area. A large amount of Na possibly causes point defects in Si. This study sheds new light on the c-Si PID mechanism.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308 with the National Renewable Energy Laboratory. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

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