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Kinetics Study on Carrier Injection-Induced Degradation and Regeneration at Elevated Temperature in p-Type Cast-Monosilicon Passivated Emitter Rear Contact Solar Cells

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Herein, the degradation and regeneration processes of p-type cast-monosilicon passivated emitter rear contact solar cells are investigated, by taking open-circuit voltage as a measure for the light- and elevated-temperature-induced degradation (LeTID) and regeneration extent. Degradation and regeneration are triggered by current injection and light soaking at the same temperatures. Then, an Arrhenius plot, derived from the proposed model, is used to extract the degradation and regeneration rate constants of LeTID during both current injection and light-soaking processes. The activation energies of degradation processes are calculated to be (0.790 ± 0.064) and (0.828 ± 0.013) eV for current injection and light soaking, respectively. The corresponding activation energies for regeneration processes are (1.059 ± 0.112) and (1.179 ± 0.070) eV, respectively. Notably, the similar activation energies indicate that the root cause of the LeTID induced by current injection or light soaking is the same. In addition, an exponential dependence of the rate constants upon the injection current values during the whole degradation and regeneration cycle induced by current injection is observed. These results are not only significant for understanding the kinetics of LeTID but also can shed light on effective LeTID suppression method in the photovoltaic industry.

1. Introduction

Crystalline silicon including multicrystalline silicon (mc-Si) and Czochralski silicon (Cz-Si) has been widely used as solar cell substrate material. Recently, a rapid developing technology, namely, cast-monosilicon (cm-Si), has taken a certain market share.[1] Due to the development of a proper seed arrangement and the use of functional grain boundary technology, the propagation of dislocations in cm-Si could be effectively suppressed,[2,3] resulting in the conversion efficiency of cm-Si passivated emitter rear contact (PERC) solar cells exceeding 23%. In addition, the growth process of cm-Si is fully compatible with that of mc-Si, which is suitable for mass production.

Light- and elevated-temperature-induced degradation (LeTID) is a significant problem in PERC solar cells. Ramspeck et al.[4] first reported LeTID, which refers to a degradation of the efficiency of crystalline silicon solar cells under illumination at elevated temperatures. Different from light induced degradation in Cz-Si, LeTID could be explained neither by BO complexes nor by iron–boron (FeB) pairs.[4,5] One significant observation reported by Chan et al. and Bredemeier et al. gives a clue that the LeTID extent will increase with a higher peak firing temperature (>650 °C),[6,7] which indicates that the mechanism of LeTID could be related to some kinds of fast diffusers inside the silicon bulk such as interstitial metal atoms or interstitial hydrogen. In addition to that, various studies suggested that interstitial hydrogen, which is released from the passivation layer into the silicon bulk, plays a major role in the LeTID defect formation and/or activation.[8,9] LeTID has also been demonstrated to be activated by excess carrier injection through illumination or voltage bias,[10] hence often referred to as carrier-induced degradation (CID).[11] Moreover, Chan et al. and Vargas et al. reported that dark annealing is able to trigger LeTID and alter the defect behavior during subsequent light soaking.[12,13] More recently, it has been demonstrated that the LeTID defect is present in Cz-Si, mc-Si, FZ-Si, and even in n-type Si wafers with electrical parameters in a similar range.[14–16] However, the exact root cause of LeTID is still unknown.

Cm-Si is more suitable for the LeTID investigation as compared with mc-Si and Cz-Si. Mc-Si contains a large number of crystallographic defects, which may affect the accuracy of electrical performance testing. Furthermore, crystallographic defects may change the behavior of LeTID participants (H, vacancies, self-interstitial silicon atoms, etc.) and thus change the kinetics of LeTID formation. On Cz-Si, however, the lower LeTID defect

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DOI: 10.1002/solr.202100035

density compared with cast-silicon materials and the presence of boron−oxygen related defects affect the accurate LeTID characterization. Therefore, cm-Si with low interstitial oxygen concentration and low crystallographic defect density is a suitable material for studying the dynamics and mechanism of LeTID. As a widely used method to suppress LeTID during mass production is the combination of current injection and low-temperature annealing, understanding the impact of current injection on the LeTID mechanism is of similar importance as examination under illuminated conditions. In this study, we use p-type cm-Si PERC solar cells to investigate the kinetics of current injection-induced and light soaking-induced degradation and regeneration at elevated temperatures to give some insights into LeTID mechanism.

2. Results and Discussions

Figure 1 shows the evolution of the normalized defect density of $78 \times 78\ \text{mm}^2$ cm-Si PERC solar cells during 1.3 suns light soaking or 12 A current injection at different temperatures in the range from 110 to 230 °C. To ensure the complete regeneration of V_{oc} for the accuracy of modeling, the temperature is set to be quite higher than that of standard stability tests, which is 80 °C.

It is obvious that both current injection and light soaking at higher temperatures lead to higher degradation/regeneration rates and lower maximum NDD. Moreover, there is no degradation but only improvement in V_{oc} when cells are treated with 12 A or 1.3 suns at 230 °C. This is in agreement with previous reports of light soaking and dark annealing experiments with lifetime samples.[13] It gives us a clue that LeTID is highly temperature dependent, for both degradation and regeneration parts. Furthermore, there should be a critical temperature and carrier injection concentration, for which the regeneration part will start to be dominating. In our experiment, the critical point is 200 °C with 1.3 suns light soaking or 230 °C with 12 A current injection. Obviously under the treating conditions of 12 A and 1.3 suns at 230 °C, the regeneration occurs much faster than the degradation, so degradation seemingly vanishes, therefore, leading to the notable V_{oc} improvement. It could be due to the more pronounced temperature dependence of the regeneration process with larger activation energy. Please note that although the maximum NDD at 110 °C is very similar between current injection and light-soaking conditions, their reaction rates are quite different.

Due to the notable regeneration of V_{oc} for both light soaking and current injection cells, it is reasonable to consider a three-state model. The equations are given as follows.

$$\frac{\mathrm{d}N_{\mathrm{A}}(t)}{\mathrm{d}t} = R_{\mathrm{deg}} N_{\mathrm{A}}(t) \tag{1}$$

$$\frac{\mathrm{d}N_{\mathrm{D}}(t)}{\mathrm{d}t} = R_{\mathrm{deg}} N_{\mathrm{A}}(t) - R_{\mathrm{reg}} N_{\mathrm{D}}(t) \tag{2}$$

$$\frac{\mathrm{d}N_{\mathrm{R}}(t)}{\mathrm{d}t} = R_{\mathrm{reg}} N_{\mathrm{R}}(t) \tag{3}$$

$$N_{\mathrm{D}}(t) = \frac{N_{\mathrm{A,0}} R_{\mathrm{deg}}}{R_{\mathrm{deg}} - R_{\mathrm{reg}}} [\exp(-R_{\mathrm{deg}} t) - \exp(-R_{\mathrm{reg}} t)] \tag{4}$$

where N_{A}, N_{D}, and N_{R} denote the normalized density of the initial, degraded, and regenerated states of LeTID defect, according to the three-state model. For simplified analysis, we use the maximum normalized defect density $\mathrm{NDD_{max}}$ to represent $N_{\mathrm{A,0}}$, which is the normalized density of N_{A} before LeTID, t is the treatment duration, and R_{deg} and R_{reg} are the rate constants of degradation and regeneration, respectively. The derived two exponential fits are shown in Figure 1. Notably, the average determination coefficients (r^2) of the fitting are 0.965 for light-soaking cells and 0.943 for current injection cells, respectively, indicating quite good fits.

Please note that in our model, we only consider one single defect to induce LeTID, and both the activation and deactivation of this defect are triggered once cells are light soaked or current injected at a certain temperature. The assumption of one single defect responsible for LeTID is in agreement with other reports,

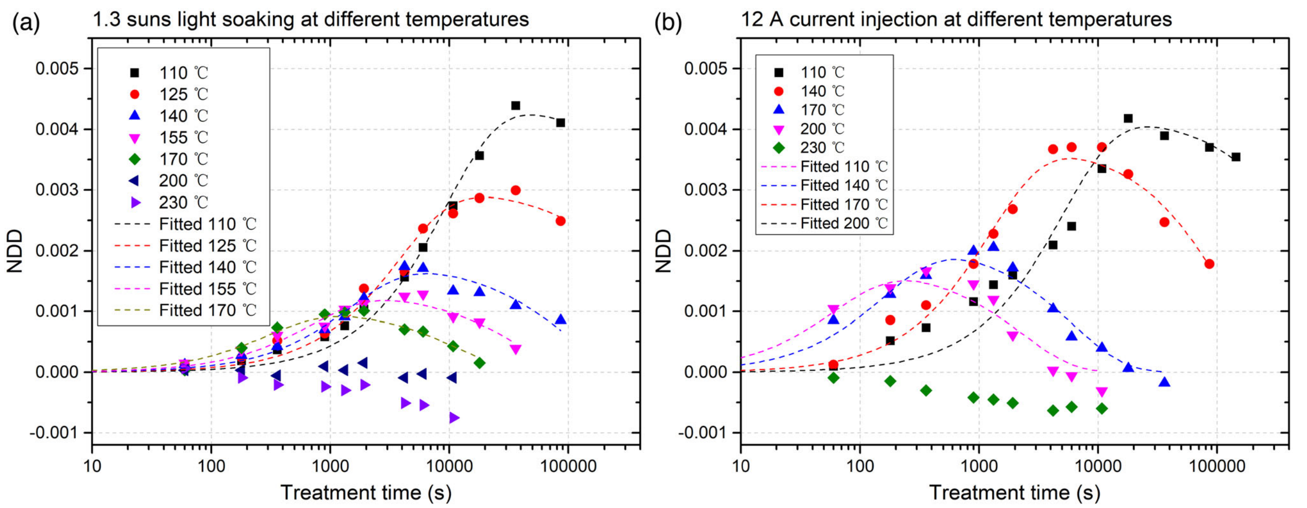

Figure 1. The evolution of the normalized defect density under a) 1.3 suns light soaking and b) 12 A current injection at different temperatures (110, 140, 170, 200, and 230 °C).

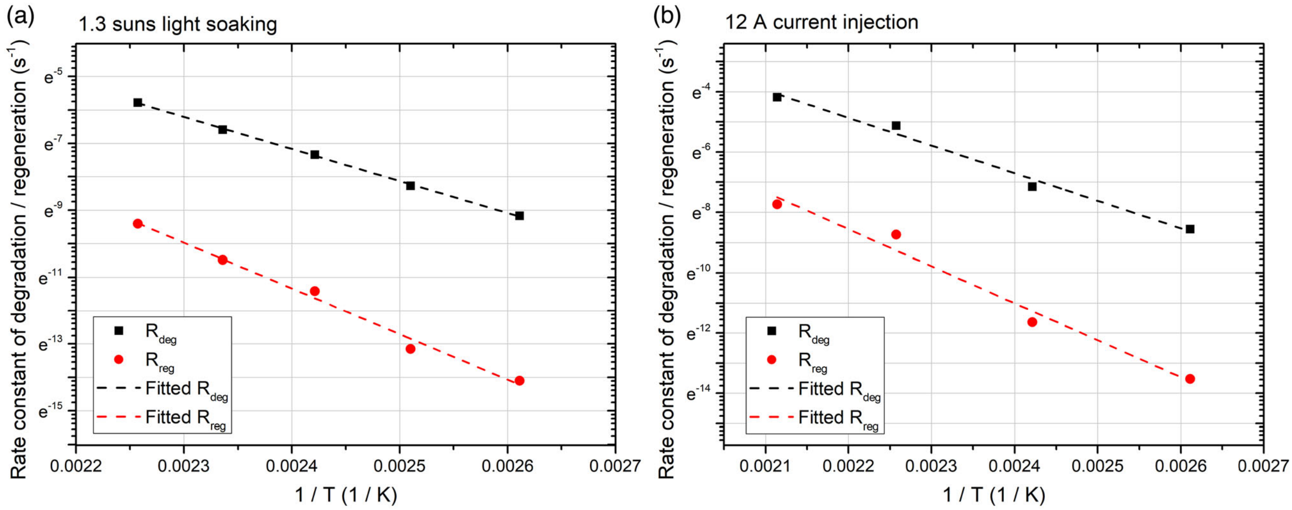

Figure 2. Fitted rate constants of degradation and regeneration caused by a) light soaking and b) current injection plotted versus the inverse temperature $1/T$ according to the Arrhenius law.

identified by lifetime spectroscopy measurements on lifetime samples.[18,19]

The activation energies of degradation and regeneration processes ($E_{deg/reg}$) are extracted from Equation (5), where $k_{deg/reg}$ is the pre-exponential factor under each condition, k_B is the Boltzmann constant, and T is the absolute temperature. Furthermore, the Arrhenius plot is shown in **Figure 2**.

$$R_{deg/reg} = k_{deg/reg} \exp\left(-\frac{E_{deg/reg}}{k_B T}\right) \tag{5}$$

The activation energies obtained under light-soaking conditions are (0.828 ± 0.013) eV for the degradation process and (1.179 ± 0.070) eV for the regeneration process, whereas under current injection condition are (0.790 ± 0.064) and (1.059 ± 0.112) eV, respectively. The similarity between the activation energies of light-soaking and current injection conditions may also give us a clue that the degradation and regeneration processes of both treatments are caused by the same defect. It is to say that the activation of defect precursor only depends on the injected excess carrier density, rather than the method of injection. Another interesting observation in Figure 1 shows that at 200 °C, there is almost no degradation in light-soaking cells, whereas a notable V_{oc} degradation and regeneration cycle is observed in current injection cells. As the temperature stays the same, this difference should be caused by different carrier injection densities induced by either light soaking or current injection, i.e., LeTID can be significantly modulated by carrier injection density. Please note that the activation energies obtained from our experiments are somewhat different from others claimed by Vargas et al.[13] with $E_{deg} = (1.08 \pm 0.05)$ eV and $E_{reg} = (1.11 \pm 0.04)$ eV. Nevertheless, the degradation and regeneration processes they conducted are under dark annealing conditions, and the mc-Si lifetime samples they used are without electrodes and back surface field, which could cause a reduced level of excess carrier density during the experiments. Therefore, it will lead to different LeTID evolutions and hence different extracted activation energies.

Furthermore, Bredemeier et al. reported the values $E_{fast} = (0.89 \pm 0.04)$ eV and $E_{slow} = (0.93 \pm 0.06)$ eV for the fast and slow lifetime degradation processes of mc-Si wafers under light-soaking conditions,[19] respectively. The model they proposed is based on the transformation of configuration between $M_i{-}X$ and $M_i{-}X^*$, which are both recombination active and responsible for the slow- and fast-lifetime degradation processes, respectively. However, only one single defect is considered to induce LeTID in our model, the same as once proposed in literatures.[10,18,19] Notably, there is almost no lifetime regeneration in their samples, but the regeneration part in our experiments is evident enough to make a difference on the extracted activation energies.

It should be noted that the cm-Si PERC solar cells used in our experiments contain much less grain boundaries and dislocations as compared with mc-Si samples, and the different activation energies we obtained could somehow be explained by the involvement of crystallographic defects in the formation and dissociation of the LeTID defect. It is reported that the extent of LeTID is reduced in the vicinity of grain boundaries if compared with its extent in intragrain regions. In high recombination areas, LeTID is not evident.[14,20,21] Furthermore, the obviously slower degradation and regeneration rates at a grain boundary as compared with intragrain is observed by Jensen et al., and they claimed that it is related to an inhomogeneous LeTID defect distribution in the vicinity of grain boundaries.[22] Therefore, the presence of crystallographic defects may inhibit the activation of the LeTID defect, for example, by capturing the possible precursor (interstitial hydrogen, metal atom, self-interstitial, or vacancy)[8,14] of the LeTID defect during illumination at elevated temperatures.

Figure 3a shows the evolution of the normalized defect density under different current injections (2, 6, 10, 14 A) at 170 °C, depicting a regular pattern that higher injection current causes both higher $R_{deg/reg}$ and lower degradation extent. In particular, as shown in Figure 3b, an exponential dependence of $R_{deg/reg}$ upon injection current value is observed. The correlation between injection current and $R_{deg/reg}$ at 170 °C is shown as follows.

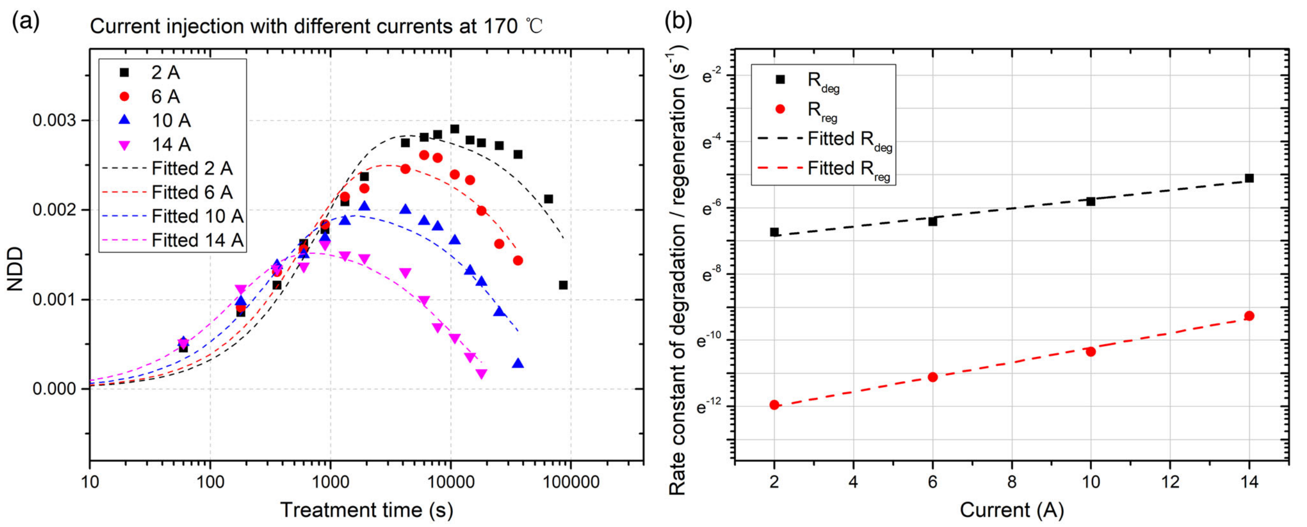

Figure 3. a) The evolution of the normalized defect densities injected with different currents (2, 6, 10, and 14 A) at elevated temperatures (170 °C) and b) fitted rate constants of degradation and regeneration plotted versus the injection current values.

$$R_{deg/reg} = \exp\left(a_{deg/reg} \times I + b_{deg/reg}\right) \tag{6}$$

where $a_{deg/reg}$ and $b_{deg/reg}$ refer to two determining factors, I is the applied current, and $a_{deg} = (0.138 \pm 0.016)$ A^{-1}, $a_{reg} = (0.221 \pm 0.012)$ A^{-1}, $b_{deg} = (-7.124 \pm 0.145)$, and $b_{reg} = (-12.443 \pm 0.107)$, as shown in Figure 3b.

However, Bredemeier and Kwapil et al. claim a nearly linear dependence of R_{deg} on the applied illumination intensity[19] and injected Δn,[10] respectively. Several factors could cause this difference. The first and most important one is the ignorance of regeneration kinetics in their model, and regeneration part should induce important effects in deriving R_{deg}. The second one may be due to the higher injection density that we use. Future experiments could focus on the dependence within different ranges of injection densities to verify this relationship.

As discussed earlier that LeTID is temperature dependent and injection density dependent, one interesting observation in Figure 1 is that the light-soaking cells show no degradation but current injection cells do at 200 °C, although the injection density of 12 A is higher than 1.3 suns. Further studies are required to explain this observation in detail, especially focusing on the variations of current and light intensity at 200 °C to examine at which point the degradation really vanishes.

Based on the researches in lifetime structure samples, our results give some complementary understanding into kinetics of current injection-induced degradation and regeneration in p-type cm-Si PERC solar cells, which may provide some insights in eliminating LeTID through current injection methods in the photovoltaic industry.

3. Conclusion

In this study, we choose p-type cm PERC solar cells, which are suitable samples to investigate LeTID, to conduct the current injection-induced and the light soaking-induced degradation and regeneration at elevated temperatures. Considering both the degradation and regeneration parts, a two-exponential fitting model is used to extract the rate constants and activation energies of each process induced by current injection and light soaking, respectively. The results reveal very similar activation energies. The activation energies of degradation are (0.790 ± 0.064) and (0.828 ± 0.013) eV for current injection and light soaking and that of regeneration are (1.059 ± 0.112) and (1.179 ± 0.070) eV with corresponding treatments. This phenomenon suggests that both current injection and light soaking should activate the same defect responsible for LeTID. Furthermore, an exponential dependence of the degradation and regeneration rate constants on the current value applied to cells is observed (in the range from 2 to 14 A), which indicates that the rate of LeTID is dependent on the injected excess carrier density. The results in our article expand previous results on lifetime samples and would be valuable for understanding the LeTID mechanism, which could lead to effective suppression methods toward LeTID.

4. Experimental Section

Several neighboring 156 × 156 mm^2 p-type cm-Si wafers with resistivity of 1.0 ± 0.1 Ω cm were chosen to undergo industrial PERC solar cell processing, including cleaning, acid texturing, phosphorus diffusion (with an average emitter sheet resistance of 130 Ω sq^{-1}), phosphorous silicate glass removal, passivation layer deposition, and contact firing (850 °C/1 min), which were done by Chint Co, Ltd. The final thickness of these PERC solar cells was 180 ± 2 μm. In our experiment, these cells were laser cleaved into 78 × 78 mm^2 and split into two groups of sister tokens for ease of further treatments.

To conduct light soaking, these cleaved cells were placed on a heating stage at a certain temperature and illuminated with a halogen lamp. To conduct current injection, cells were placed on a copper plate, which was connected with a current source and heated by a heating stage. Please note that the current injection treatment was conducted in a dark room with the illumination intensity lower than 0.1 W m^{-2}, measured by a solar power meter SM206, to minimize the effect of photogenerated carriers on experiment accuracy. The open-circuit voltage (V_{oc}) was collected by Sinton Suns-V_{oc} tester before and during light soaking or current injection treatment with a regular interval, at the temperature (26 ± 0.3 °C).

Then, the normalized defect density (NDD) was calculated from measured V_{oc}, according to $\text{NDD}(t) = \frac{1}{\exp[qV_{oc}(t)/k_B T]} - \frac{1}{\exp[qV_{oc}(t=0)/k_B T]}$,[17] to characterize the activation and deactivation of LeTID defect. All the experiments were continuously conducted once started to exclude the influence of dark storage. Please note that when the temperature at the center of $78 \times 78\,\text{mm}^2$ samples was set to values from 110 to 230 °C, the lateral uncertainty ranged from 1.5 to 3 K, and when the illumination intensity at the center of the $78 \times 78\,\text{mm}^2$ samples was set to 1.3 suns, the lateral uncertainty was about 0.15 suns. Cells from Group I were current injected with a current of 12 A or light soaked with a light intensity of 1.3 suns at different temperatures (110, 140, 170, 200, 230 °C), to compare the difference between current injection-induced and light soaking-induced degradation and regeneration. Cells from Group II were current injected with different currents (2, 6, 10, 14 A) at a temperature of 170 °C to examine the dependence of degradation and regeneration upon applied current values. Notably, the initial V_{oc} of these cleaved cells for current injection was 655.6–656.9 mV and for light soaking was 656.1–657.7 mV. The corresponding initial pseudoefficiency was 20.55–20.64 and 20.52–20.66%.

Acknowledgements

Z.H. and Q.H. contributed equally to this work. The authors would like to thank Lingxin Fang at Zhejiang Chint Solar Co., Ltd., for providing PERC solar cells. This work was supported by the National Natural Science Foundation of China (nos. 62025403, 61974129, 61721005, and 62004173), National Key Research and Development Project (2018YFB1500401 and 2020YFB1506502), and Visiting Scholars Foundation of State Key Laboratory of Silicon Materials (SKL2020-01).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Keywords

carrier injection, cast-monosilicon, light- and elevated-temperature-induced degradation (LeTID), passivated emitter rear contact solar cells, photovoltaics

Received: January 14, 2021
Revised: April 7, 2021
Published online:

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