Carrier-Induced Degradation in Monocrystalline Silicon: Dependence on the Temperature and Irradiance

Hailing Li, Xinxin Wang and Wenjing Wang

1 The Key Laboratory of Solar Thermal Energy and Photovoltaic System, IEE-CAS, No. 6 Beiertiao Zhongguancun, Haidian District, Beijing, China
2 University of Chinese Academy of Sciences, No. 19 Yuquan Road, Shijingshan District, Beijing, China
Email: lihailing@mail.iee.ac.cn

Abstract. The dependence of the carrier-induced degradation on the temperature and irradiance is studied. The stability of samples after accelerated degradation and regeneration at different temperature and irradiance are studied also. Minority carrier lifetime and normalized defect density are used to characterize the degradation and regeneration kinetics. The mechanism of temperature and irradiance on degradation is studied and discussed.

1. Introduction
With the increase of market share of PERC (Passivated Emitter and Rear Cell), a new degradation phenomenon called CID (Carrier-Induced Degradation) has been found, which is different from BO-LID (Light-induced Degradation) in the following aspects: (1) higher degradation, the conversion efficiency of mono-crystalline silicon PERC cells will generally decline by 3-5%, and that of multi-crystalline silicon PERC cells will generally decline by 7-10%; (2) longer time required for the degradation and regeneration, which may take 100h at 75°C, and 700h for subsequent regeneration for multi-crystalline silicon [1, 2]. With the long timescale, the regeneration will take place on a timescale equivalent to several decades in field; (3) different from BO defect, it needs a high temperature to activate [3-5], so it is also called Light elevated Temperature Induce Degradation (LeTID) [1, 3, 6, 7]. The mechanism of CID has been widely studied and is still unclear [1-7]. It is clear that CID is independent of interstitial oxygen and dopant boron concentration. Under irradiation and temperature, it is found that the lifetime of bulk decreases significantly. This phenomenon is not only found in multi-crystalline silicon, but also in CZ and FZ silicon. At the same time, it is found that the degradation and regeneration is related to the firing process (peak firing temperature and cooling rate). Some people think that the metal precipitates will be dissolved again and transit into mobile metal atom during the high-temperature firing process, and the metal atom is captured by another kind of uniformly distributed impurity to form recombination inactive complexes, which are separated under high-temperature and irradiation to form metal atoms with active recombination. The subsequent diffusion of metal atoms to the surface or grain boundary are considered to be the root cause leading to regeneration [8]. The study of temperature and injection related lifetime analysis identified possible defects: Ti, Mo, and W [3]. This model usually used in multi-crystalline silicon.

Another widely accepted model is the effect of hydrogen and its interaction with bulk defects [7, 9]. Interstitial hydrogen can be introduced from different concentrations of hydrogenation coatings,
such as SiNₓ:H and AlOₓ:H [9]. It is recognized that diffusion of hydrogen in bulk silicon depends on the injection of a high concentration of hydrogen at a high temperature. It is observed that the degradation can be activated once the peak temperature of rapid firing process exceeds ~598 ℃, which is about the temperature of hydrogen release from silicon nitride coating.

In order to study CID mechanism on boron-doped Cz-Si, the influence of temperature and irradiance was studied. We examine the carrier lifetime degradation under different illumination and temperature of boron-doped Cz-Si material, and the stability was checked also.

2. Experimental Setup
0.5-1 Ω·cm p-type boron-doped mono-crystalline wafers, selected from neighbouring locations in the ingot, were used to fabricate symmetrical lifetime structures. Wafers underwent texturing to a final thickness of about 170±10 µm. A phosphorus diffusion was performed on all wafers in a POCl₃ tube furnace resulting in emitter on both sides. Hydrogenated silicon nitride (SiNₓ:H) dielectric layers were deposited on both sides. Wafers were fired with peak wafer temperature more than 700℃ at a constant belt speed. Wafers were laser cleaved into tokens (50 mm × 50 mm) and grouped to form “sister” sets. The high illumination intensity and temperature were used to accelerate defect formation and regeneration by Jingsheng lighting annealing furnace. In this equipment, the light intensity is 20 suns, and the spectral distribution is a monochromatic LED light with a peak wavelength of 850 nm. The temperature of silicon wafer can be controlled between 50-200 ℃ during irradiation.

The low illumination intensity and temperature were used to check the stability by light soaking furnace provided by Xi’an Zhongsen company. Light soaking furnace has AM1.5 simulated light source, 1 sun intensity, and the temperature of silicon wafer can be controlled at 50-150 ℃.

After irradiation for a certain period of time, the wafers are taken out from the irradiation condition for testing. After the test, they are put into the furnace again for irradiation and heating treatment.

The degradation and regeneration of silicon wafer is characterized by the minority carrier lifetime. The lifetime test is conducted by the quasi-static photoconductivity method with wct-120 equipment of Sinton company. If there is no special specification, the lifetime means the value when the excess carrier concentration Δn=5×10¹⁵ cm⁻³. The normalized defect density (NDD) is calculated by the following formula:

\[
NDD(t) = \frac{1}{\tau_{\text{eff}(t)}} - \frac{1}{\tau_{\text{eff}(0)}}
\]

The initial lifetime before the start of degradation is \(\tau_{\text{eff}(0)}\), and the lifetime after irradiation time \(t\) is \(\tau_{\text{eff}(t)}\). By calculating NDD, the difference caused by different wafer sources can be eliminated as much as possible.

3. Dependence on the Temperature and Irradiance

3.1. Dependence on the Temperature
As shown in figure 1, degradation and regeneration occur under all the three temperature conditions. And degradation become serious at low temperature. At the temperature of 110 ℃, lifetime degraded to 75% of initial value. While at the high temperature of 150 ℃, it shows only a slight degradation, and the lifetime recovers rapidly. After recovering, the lifetime improves continually and significantly by about 20%. That means that degradation can be impeded by high temperature. In addition, it can be seen from the figure that with the increase of temperature, both the degradation rate and regeneration rate are improved. On other words, the effect on degradation and regeneration is different, indicating that the competition relationship between the degradation and regeneration is affected by temperature, which results in different degradation extent. This explained the reason why high temperature can hamper degradation. And the different dependence of temperature on degradation rate and regeneration rate also indicates that the diffusion substances causing the degradation and regeneration may be different.
Figure 1. Effective lifetime $\tau_{\text{eff}}$ (a) and normalized defect density NDD, (b) versus the light annealing accumulated times at 50% light power and different temperature. 5 cm × 5 cm silicon wafers are placed in a light annealing furnace under the following conditions: 50% fixed irradiation power, the temperature of the silicon wafer is 110 °C, 130 °C and 150 °C. Figure 1a shows the change of minority carrier lifetime, and figure 1b shows the change of normalized defect density (NDD).

For the reason why wafer lifetime can be improved more than initial value after degradation and regeneration, we think H in the bulk silicon may play a role in passivation of other defects in the silicon, thus improving the minority carrier lifetime.

3.2. Dependence on the Irradiation
Wafers were placed in light annealing furnace at 135 °C (± 5 °C) with irradiation intensities of 90%, 50% and 30% power separately. As shown in figure 2, at the same temperature of 135 °C, at different irradiation power of 90%, 50% and 30%, the silicon wafers under 90% and 50% power show a similar reaction process, with the same lowest degradation value and reaction rates, only showing a little difference at the last stage of regeneration. In contrast, under 30% power wafer shows a similar lowest degradation value (the small difference is considered to be related to the temperature difference of ± 5 °C), but the degradation and regeneration rate is significantly slower.

Figure 2. (a) Effective lifetime $\tau_{\text{eff}}$ and (b) normalized defect density NDD versus the light annealing accumulated times at 135 °C and different irradiation power.

The excess carrier concentration $\Delta n$ is related to the degradation. Therefore, with the change of irradiation intensity, the excess carrier concentration changes. In the study of this paper, there is an irradiation intensity threshold. When irradiation intensity strong than 50%, more excess carrier concentration resulted same reaction rate. Considering that CID is essentially a diffusion limiting
kinetic, it is speculated that the diffusion rate of defect precursor and defect related species will be the limiting factor under a certain excess carrier concentration.

3.3 Stability Study
In order to study the stability of lifetime after accelerated degradation and recover at different temperature irradiance treatment, we put the wafers into light soaking furnace with condition of 1 sun @ 75 °C for about 100 hours.

Figure 3 shows the change of minority carrier lifetime of silicon wafer under light soaking. For comparison, the lifetime change of untreated blank sample (wafer without degradation and regeneration kinetics) was given. It can be seen from the figure that, compared with the untreated blank sample, all the samples undergoing light annealing process showed good stability. The maximum degradation rate of the blank samples reaches 36%, while the maximum degradation rate of the treated samples is 8%(90% power@140 °C), indicating that a large number of recombination active defects complex transited into inactive stable state which is stable under room temperature. It is very interesting that the lifetime of the sample treated under low irradiance and low temperature is improved continuously under light soaking. While that of the sample treated with relatively high irradiance and temperature (90% power@140 °C and 50% power@135 °C), showed second degradation and then gradually regenerated. The sample treated under 90% power@140 °C showed higher degradation than the one treated under 50% power @ 135 °C.

Figure 3. Stability of lifetime of silicon wafers under light soaking (blank sample means the one without light annealing treatment).

3.4 Analysis and Discuss
By heating and irradiating silicon wafers in a light annealing furnace, the degradation and regeneration of silicon lifetime are found, which was called carried induced degradation. It is found that the influence of temperature and irradiance on the dynamic of degradation and regeneration is different. The temperature affects the degradation and regeneration reaction rates, as well as the degradation amplitude. While the irradiance only affects the reaction rates, but does not affect the degradation amplitude. It is found that there seems to be an irradiation threshold, and higher irradiation intensity does not lead to faster reaction rate when it exceeds threshold.

As discussed before, subsequent to fast-firing, the majority of hydrogen exists in molecular form (H₂A) leaving only a small fraction of B-H [10]. This B-H could be state A; non-recombination active but ready to supply defect precursors (interstitial H) during future processing. The dissociation of B-H pairs in carrier injection (e.g., illumination) reduces the activation energy for dissociating B-H from 1.76 ± 0.05 eV to 1.1 ± 0.1 eV [11]. One possible mechanism suggested for this is a change in the charge state of hydrogen from H⁺ to H° thus allowing it to more easily to escape from B⁻ after
dissociation [12]. Consequently, the H° that escaped could then diffuse and reach another species to cause the recombination-active defect under illumination (state B) and participate the regeneration of defect. This regenerated defect is state C and considered to be more stable than state A and possibly represents a more stable bulk lifetime for the silicon wafers. The role of the different hydrogen species and their response to temperature and illumination potentially explains some other observations within the literature.

In our experiment, high temperature promotes regeneration and inhibition degradation. So if H° resulted in recombination active defect complex, high temperature and high light intensity would accelerate the formation and diffusion of H°, and then speed the degradation kinetics. This is corresponding to our experiment results. However, this cannot explain why there are different degradation extents at different temperatures, and the degradation extents are the same at different light intensities. At the same time, it cannot explain why the samples with high temperature and high light intensity show worse stability in the subsequent light soaking. Because high temperature and high light intensity result in higher concentration of H°, and the stable state of H°C formed by H° is considered to be stable in a light soaking at 1 sun @ 75 °C.

So we speculate that there should be more than one degradation mode in the mono-crystalline silicon CID. Both BO defect complex and H-related defect complex co-exist in silicon bulk material. High temperature or light intensity promote the formation of H°, accelerates degradation and regeneration, but on the other hand, it also aggravates the possibility of BO dissociation, which leads to BO recombination active complex transit into metastable state, so that in the subsequent light soaking, they degrade again. This also explains why the higher the temperature, the slighter the degradation. The possible degradation and regeneration model for mono crystalline silicon is shown in figure 4.

4. Conclusions
Temperature will change the competitive relationship between degradation and regeneration, which will lead to the change of the lowest value of degradation, as well as degradation and regeneration speed; irradiance will not change the competitive relationship between degradation and regeneration, but will influence the degradation and regeneration speed. That means that it its possible temperature and irradiance play different roles in mono-crystalline silicon CID. At the same time, it is found that samples under light annealing at different temperature and irradiance shows different stability when suffering light soaking at 1 sun @ 75 °C. 3-state model and the presence of hydrogen can explain the influence of irradiation and light intensity on the reaction speed, but can’t explain the influence of temperature on the degradation extent and the light soaking stability. We proposed degradation and
regeneration model for mono crystalline silicon that two different degradation State coexist, state B with H participation and state B’ without H participation.

Acknowledgments
Authors would thanks to the support from National Key R&D Program of China (2018YFB1500900) and K.C.Wong Education Foundation.

References
[1] Friederike K, Peter E, Hans-Christoph P, Andrey S, Thomas L, Florian S, Matthias B, Andy S, Kai P, Johannes H and Jörg W 2015 Solar Energy Materials & Solar Cells 142 83-6
[2] Chan C, Tsun H, Malcolm A, David N, Alison M, Brett H, Ran C and Stuart W 2017 Solar Rrl 1 1600028
[3] Nakayashiki K, Hofstetter J, Morishige A, Li T, Needleman D and Jensen M 2016 IEEE Journal of Photovoltaics 6 1-9
[4] Chan C, Payne D N R, Hallam B J, Abbott M D and Wenham S R 2016 IEEE Journal of Photovoltaics 99 1-7
[5] Bredemeier D, Walter D, Herlufsen S and Schmidt J 2016 silicon Energy Procedia 92 773-778.
[6] Eberle R, Kwapil W, Schindler F, Schubert M C and Glunz S W 2016 Physica Status Solidi (RRL)-Rapid Research Letters 10 861-5
[7] Jensen M A, Morishige A E, Hofstetter J, Needleman D B and Buonassisi T 2017 IEEE Journal of Photovoltaics 7 980-7
[8] Niewelt T, Kwapil W, Selinger M, Richter A and Schubert M C 2017 IEEE Journal of Photovoltaics 7 1197-202
[9] Sheoran M, Kim D S, Rohatgi A, Dekkers H F W, Beaucarne G and Young M 2008 Applied Physics Letters 92 172107
[10] Voronkov V V, Falster R, 2017 Physica Status Solidi b1600779
[11] Zundel T and Weber J 1991 Physical review. B, Condensed matter 43 4361-72
[12] Seager C H and Anderson R A 1991 59 585-7