



Kinetics of carrier-induced degradation at elevated temperature in multicrystalline silicon solar cells



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ARTICLE INFO

Keywords:

Multicrystalline silicon solar cells
Light- and elevated temperature-induced degradation
Carrier-induced degradation
Kinetics

ABSTRACT

The degradation kinetics of multicrystalline silicon solar cells and wafers at elevated temperature (often termed “LeTID”) depend on the specific temperature and injection conditions. We apply different forward biases in the dark at a constant temperature of $\sim 75^\circ\text{C}$ to industrial passivated emitter rear contacted (PERC) solar cells fabricated on p-type multicrystalline wafers from a variety of material producers and determine the degradation rate constant in dependence of the excess carrier density at the p-n junction. We find that whereas the specific material properties influence the degradation extent, the degradation rate constant is comparable for all materials but depends on the excess carrier concentration. This implies involvement of one electron in the rate-limiting step of LeTID defect formation. The result not only is an important contribution to elucidate the physical mechanism underlying LeTID, but can also be used as a guideline for devising degradation tests of multicrystalline silicon wafers and solar cells.

1. Introduction

Light- and elevated temperature-induced degradation (LeTID) of multicrystalline silicon solar cell parameters and carrier lifetime has received significant attention due to its negative impact especially on highly efficient passivated emitter and rear contact (PERC) solar cells [1]. Besides illumination, the characteristic defect degradation can also be observed upon current injection, pointing towards a carrier-induced degradation (CID) mechanism [2]. Apart from that, the defect creation mechanisms as well as the participating components are still unclear: multicrystalline silicon wafers from different material suppliers differ in the degradation extent [2,3] and gettered wafers degrade less than ungettered sister samples [4], indicating that some impurity present in the starting material is involved. In addition, the degradation extent is strongly affected by solar cell processing steps: for example, a higher firing temperature peak leads to stronger degradation [3,5,6]. The temperature ramps are crucial for the degradation extent with fast temperature ramps (typical e.g. for fast firing ovens) causing stronger degradation, whereas slow temperature ramps decrease or even fully suppress LeTID, even for high peak temperatures [7]. A similar result can be obtained when adding a second fast-firing step featuring a lower peak temperature [6]. Also, the surface passivation layer has been shown to influence the degradation and regeneration behaviour [8].

The necessity of a high peak firing temperature for observation of LeTID has led to the hypothesis that the responsible impurity is initially

present as precipitates, which need to be dissolved in order to be able to act as LeTID “precursor” [5]. Either as an alternative or a complementing explanation to this hypothesis, the presence of hydrogen seems to be necessary for LeTID activation [8]. Either way the fact that the carrier lifetime degrades over an extended period of time suggests an interaction between two or more components, which undergo a transformation under degradation conditions. It is likely that this transformation is either related to the dissociation of an impurity complex (a prominent example for such a mechanism is the reaction $\text{Fe}^+\text{B}^- \rightarrow \text{Fe}_i^+ + \text{B}^-$ under illumination) or the formation of one. Please note that several authors already have ruled out the possibility that the known metastable defects Fe_i/FeB and boron-oxygen cause LeTID [1,2,9].

In addition to the degradation, it is observed that after a certain time, regeneration of the solar cell parameters / carrier lifetime occurs [2].

Degradation and regeneration kinetics strongly depend on the injection conditions and the temperature [2,10]. It is known that higher injection and/or higher temperature accelerate the degradation / regeneration cycle [2,10]. This can be exploited for very fast – and potentially industrially feasible – regeneration processes [10,11]. Recently, another significant influence has been identified: As Chan *et al.* showed, annealing LeTID-susceptible samples in the dark in the order of minutes to hours prior to illumination at elevated temperature alters the subsequent degradation and regeneration behaviour significantly

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<http://dx.doi.org/10.1016/j.solmat.2017.05.066>

Received 31 March 2017; Received in revised form 23 May 2017; Accepted 29 May 2017

Available online 02 June 2017

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[12]. The underlying mechanisms appear to be nonlinear and are not yet understood: whereas dark annealing temperatures in the range of 125 °C to approx. 200 °C accelerate both degradation and regeneration compared to an untreated sample, a slightly higher temperature (~225 °C) first extremely slows down regeneration, followed by a slowed degradation and suppressed regeneration when going to even higher temperatures. *Chan et al.* noted that due to this dependence on the thermal history, studies investigating the degradation and regeneration kinetics might draw different conclusions due to even minute differences in thermal budget.

While keeping these findings in mind, studying the degradation and regeneration kinetics can provide insight into the physical processes during defect formation / annihilation. Such studies therefore are important for the identification of the root-cause defect and possibly assist in its mitigation without the necessity of complicating solar cell process adjustments.

However, the defect reaction rates as a function of carrier injection or temperature have not been quantified, yet. This work presents a study of the degradation rate constant in solar cells in dependence of the excess carrier density at the p-n junction $\Delta n(0)$ at constant temperature.

2. Approach

2.1. Samples

Full size 156 mm × 156 mm PERC solar cells were provided by an industrial manufacturer. They were processed from p-type high performance multicrystalline (HPM) silicon wafers from three different material suppliers. The materials were chosen to constitute a representative cross-section of standard commercially available wafers incorporating variations in impurity content, overall material quality and doping concentration. The three different materials are called “HPM1” (base resistivity 1.7 Ω cm), “HPM2” (2.2 Ω cm) and “HPM3” (1.9 Ω cm) in the following.

Being aware of the influences of the solar cell process steps, the process parameters were chosen to enable maximum LeTID effect. All solar cells were processed in the same run without any process variations. As no additional post-anneal was performed [12], we expect the solar cells to show the “standard” degradation under injection at elevated temperature.

2.2. Experimental

The degradation conditions of most studies of the LeTID effect published so far applied constant illumination and thus a constant electron-hole generation rate. In this approach, the concentration of excess charge carriers Δn significantly decreases over time as a result of the carrier lifetime degradation. However, in order to determine the degradation rate constant R_{deg} as a function of Δn , the excess charge carrier density should remain as constant as possible.

In this study the solar cells were therefore degraded in the dark by applying a constant voltage over time. In this approach, the excess charge carrier density at the p-n junction $\Delta n(z=0)$ was kept constant according to

$$\Delta n(0) \approx \frac{n_i^2}{N_A} \exp\left(\frac{qV_a}{k_B T}\right), \quad (1)$$

with n_i the intrinsic carrier density, N_A the doping concentration, q the elementary charge, V_a the applied voltage, k_B the Boltzmann constant and T the temperature. Although the integrated carrier density still depends on bulk carrier lifetime to some degree, with this approach carrier density variation with time is minimal.

All samples were degraded at the same temperature of 75 °C ± 3 °C.

During degradation, the current through the solar cell was

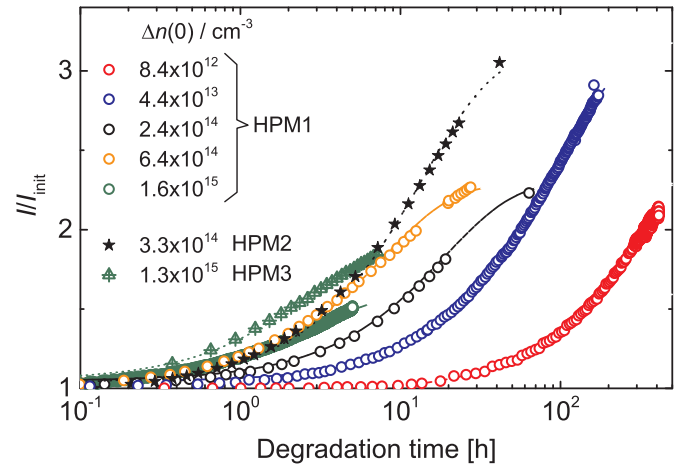


Fig. 1. Semi-logarithmic plot of the relative current increase versus degradation time. The degradation rate constant was obtained by fitting Eq. (2) to the data that is indicated by the dashed and dotted lines.

repeatedly measured. The observed increase can be entirely attributed to an increase of the saturation current density J_0 , as the exponential term of the diode equation remains constant. Following *Cuevas'* interpretation of the “recombination parameter” J_0 [13], the change in saturation current density is proportional to the change in the defect density N_t .

In addition, electroluminescence images were taken at the same time steps as the current measurements for several samples degraded at different voltages. Thus, the temporal evolution of the excess carrier density averaged over the solar cell depth could be analyzed and compared to the determined value at the p-n junction.

3. Results

In Fig. 1, exemplary current measurements of several solar cells are plotted versus the degradation time. For better comparison, all values I are normalized to the respective initial current measurement I_{init} . It is obvious that with increasing $\Delta n(0)$ (corresponding to increasing applied voltage V_a) degradation proceeds faster. Please note that the degradation at the highest voltages (green symbols) was stopped when the current limit of the power supply was reached.

In most cases, the current increase over degradation time is well described by first-order reaction kinetics, which was used to obtain the degradation rate constants R_{deg} by fitting to the proportionality

$$\frac{I}{I_{\text{init}}} \propto (1 - \exp(-R_{\text{deg}} t)). \quad (2)$$

Such fits are shown by the dashed and dotted lines in Fig. 1. Please note that it is not necessary to reach the saturation level in order to find a reliable value for R_{deg} provided that the degradation evolution has been tracked for a sufficiently long duration. On the other hand, by restricting the fit range to degradation times before saturation, the influence of the regeneration, which is believed to be a parallel process, on the current is expected to be minimal.

In a few cases the degradation behaviour showed indications of a two-stage progression with a fast and a slow component similar to the observation made by *Bredemeier et al.* [5] on lifetime samples. An example is shown in Fig. 2. Nevertheless, the exponential fit using Eq. (2) consistently yields reduced χ^2 values < 10⁻² for all experiments. In addition, when adding a second exponential to the fit function, both determined degradation rate constants $R_{\text{deg,fast}}$ and $R_{\text{deg,slow}}$ show the same general trends in dependence of $\Delta n(0)$ as R_{deg} from a Eq. (2) (an increased scatter occurred due to potential over-determination of the fits).

In Fig. 3, the degradation rate constants fitted to measured curves of

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