

## A four-state kinetic model for the carrier-induced degradation in multicrystalline silicon: Introducing the reservoir state



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### ABSTRACT

In this work, we present new insight into the multi-crystalline silicon carrier-induced defect (CID) by performing multiple degradation and regeneration cycles and further investigation on the partial recovery of mc-CID through extended dark annealing (DA). The maximum normalised defect density was found to decay exponentially with the number of cycles, suggesting that the defect precursors were slowly depleted by DA. A four-state kinetic model is proposed by introducing a reservoir state. Simulation results generated by mathematical modelling based on the proposed state diagrams exhibited good agreement with the experimental results. Extended DA on a partially recovered sample combined with simulation results suggests that the capability of defect formation through DA and the existence of the reservoir state proposed herein were the root causes for the partial recovery reported in the literature. Finally, the change in bound hydrogen state is speculated to cause the modulation of mc-CID formation. A qualitative reservoir model based on the interaction between hydrogen molecules ( $H_2$ ), boron-hydrogen pairs (B-H) and free hydrogen ( $H^+$ ,  $H^\bullet$ ) is proposed and further discussed.

### 1. Introduction

Multi-crystalline silicon (mc-Si) degradation, occurring when mc-Si wafers are subject to illumination or current injection has been an increasingly researched area in the past few years [1–5]. Its importance has risen due to its impact on the Photovoltaics (PV) industry, with mc-Si PERC solar cells set to dominate the market within the coming decade [6]. The long periods of time required for the material to degrade and eventually recover within the field [4], compounded by the severity of degradation (up to 16% relative power loss [7]) results in a significant loss in total energy yield. Furthermore, it has recently been demonstrated that the same defect can also be found on solar grade Czochralski (Cz) wafers [8,9]. Degradation appears to occur regardless of which surface passivation method is used [4], which indicates a dependence on bulk-Si material. However, the responsible species and defect formation mechanism have not yet been identified. Since the degradation can be triggered by carrier injection either from illumination or bias voltage in the dark [10,11], the degradation will be referred to in this paper as multi-crystalline carrier-induced degradation (mc-CID) rather than light and elevated temperature induced degradation (LeTID), as it is often called [2]. Nevertheless, the occurrence of such degradation has also recently been reported in Cz silicon and Float-zone (FZ) silicon [8,12]. A more accurate terminology is required

in the future.

Despite extensive research efforts in understanding mc-CID, as yet, no agreement on a kinetic state model has been reached. In contrast, a 3-state model which describes the kinetics of the BO meta-stable defect was established over a decade ago [13]. This model has greatly enhanced the understanding of the BO defect and has been referred to in numerous BO-related studies. In that 3-state model, defect precursors start at an initial state (state A) which is recombination-inactive and meta-stable. Under light soaking (LS), defect precursors transform into the degraded state (state B) which is recombination-active. Continued LS at elevated temperature then causes the recombination-active defects to transform into the regenerated state (state C), which is both recombination-inactive and stable at room temperature. However, the regenerated defect will transform back to the degraded state and subsequently to the initial state during dark annealing (DA) [14]. Some of these transitions are similar to what is observed in mc-CID; however that three state system is not able to explain all of the observed behaviours that have been reported.

Although mc-CID has a significantly longer time scale compared to BO related degradation, the behaviour under LS can be adequately described by the forward reaction in the 3-state model. For example, extensive LS causes the defect to become recombination-active and subsequently regenerate [2]. In addition, it has been shown that mc-CID

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defect formation and subsequent recovery could be accelerated by increasing temperature and/or excess charge carrier injection [10,15]. Recent studies suggest that the degradation rate constant of mc-CID at elevated temperatures possess a linearly-dependent relationship on excess charge carrier density with similar dependencies shown in BO formation rates at low illumination intensities [11,16]. Also similar to the BO system is the observation under some conditions of a two-step formation of the defect in which an initial fast degradation is followed by a slower one [17]. It has been further demonstrated that high intensity illumination can greatly accelerate the defect formation, a useful technique for studying the system given the long timescales required to complete a single cycle [10].

The response of the mc-CID system to annealing in the dark is more complicated than the BO system and remains less well understood. Early work demonstrated that the open-circuit voltage ( $V_{OC}$ ) of pre-degraded mc-PERC cells was only partially recovered by dark annealing and furthermore that full regeneration was not achievable at a range of different temperatures [18]. In addition, the degradation rates under illumination after the partial recovery were found to be significantly higher than the initial degradation. Therefore, it was suggested that the state after annealing is different from the initial state before any degradation cycle and hence not fully reversible [18]. Nevertheless, in another study the dark annealing reaction was described as defect annealing in analogy to the BO defect model [15].

On regenerated samples, dark annealing was performed and injection dependent lifetime spectroscopy (IDLS) was used to analyse the defects responsible for each cycle [19]. Due to the significant difference in  $k$ -value extracted from the first and second cycle, it was suggested that different defects were activated by DA. Dark annealing prior to degradation was shown to greatly modulate the defect formation kinetics [20]. After applying DA at temperatures below 250 °C for 2.5 h, the degradation rate and severity of degradation was increased [20].

In contrast to the defect dissociation that occurs when dark annealing the BO-related defect, recent findings have shown that DA for mc-CID could in fact cause defect formation and subsequent recovery. This was demonstrated on mc-PERC cells where the  $V_{OC}$  degraded and then recovered under DA without illumination [20]. However, surface instability was not ruled out as a potential cause in that work. Subsequent studies confirmed that DA indeed caused the formation of the mc-CID defect, independent of any surface effects, with lifetime spectroscopy finding the  $k$ -value based on Shockley-Read-Hall (SRH) statistics [21] to be similar to the light-activated defect within the error range of the study [8]. As a result, it was suggested that DA could drive the forward reaction in mc-CID. Due to this distinct property, defect formation (forward reaction) and defect dissociation (reverse reaction) in analogy to the 3-state model could happen simultaneously under DA. If true then this should be accounted for when interpreting the defect annealing results previously reported within the literature [15,18].

A final key difference between the BO defect system and the mc-CID is the response to multiple cycles of formation and mitigation. The BO system is fully reversible, meaning that multiple cycles results in a similar amount of degradation with no change in the total amount of defects within the system [22]. However in the case of mc-CID, we have recently demonstrated that multiple cycles of degradation and regeneration cause a progressive reduction in the total amount of degradation [23]. Furthermore, the extent of degradation was related to the total thermal budget applied during dark annealing. This behaviour is difficult to explain within a 3 state system and it was proposed to include a fourth state [23]. Here we expand on this concept and provide further experimental data to demonstrate the validity (and limitations) of the four-state model for mc-CID.

We describe a defect kinetic state model that accounts for various observed behaviours of mc-CID. Experimental data and simulations results are presented to demonstrate the ability of the model to reproduce the trends in effective lifetime and normalised defect density in response to a variety of DA and LS conditions. The model requires many

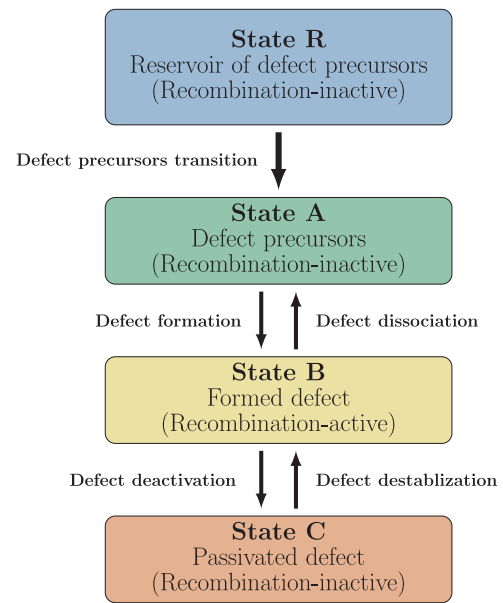


Fig. 1. Proposed four-state model for the mc-CID defect system. State A–C refer to the standard states in the original BO-LID model by Herguth et al. [13]. State R refers to the reservoir of state A precursors. Arrows represent transitions between the defect states.

unknown inputs regarding the starting concentrations and rates of change. A detailed study of each would be required to accurately determine their values, and dependencies on carriers and on temperature. In this work we focus on the ability of the model to explain the broad trends and as such we calculate the inputs to the model by fitting the simulation results to the experimental data. In doing so we demonstrate that the behaviour of mc-CID can be explained by (1) the existence of a reservoir of state A precursors in the as-fired silicon, (2) a reverse reaction between the states other than the reservoir and (3) by a single recombination active defect. This final point is determined via lifetime spectroscopy of the experimental data. Subtle differences between the simulation and the experimental data are used to highlight areas for future improvement of the model and to provide insight into the root cause of the degradation. Finally, the implications of the model for the production of stable solar cells are discussed and an explanation for the kinetics based on the complex behaviour of hydrogen within silicon crystals is proposed.

## 2. Mc-CID state model

The four-state model used to describe mc-CID in this paper is shown in Fig. 1. States A–C are similar to the traditional 3-state model used to describe the BO defect [24]. In the mc-CID model, a reservoir of recombination inactive state A precursors (state R) is added prior to state A. Under dark or illuminated annealing conditions, state A precursors are released from state R into state A. In this paper, we assume this process is irreversible (or at least that any reverse reaction is insignificant for the investigated temperature regime). Furthermore, the inclusion of a reverse reaction from state A to R was not required to describe the experimental data presented herein. Such a state could represent for example an excess supply of a particular atomic species, created during the higher temperature processing followed by rapid cooling. The proposed model does not require illumination to drive any of the reactions forward [8], however any of the transitions could be accelerated by the introduction of excess carrier injection. Finally, small but non-negligible reverse reactions have been included which allows transition from state C back to state A through state B.

In this paper we chose to simplify the degradation step to a single state transition (A→B), rather than the two step degradation reported in

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