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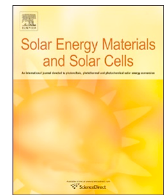

On the impact of dark annealing and room temperature illumination on *p*-type multicrystalline silicon wafers

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ABSTRACT

In the past few years, carrier-induced degradation (CID) in *p*-type multicrystalline silicon (mc-Si) has been receiving significant attention. Recently, it has been reported that this material is also susceptible to degradation under dark anneal at moderate temperatures. In the first part of this study, we investigate the impact of the dark anneal temperature on mc-Si wafers. We identify both degradation and regeneration of the effective lifetime, where higher temperatures lead to faster rates and lower degradation extent. A fitting model is developed to describe the kinetics of these processes, where the degradation and regeneration process are assumed to happen *simultaneously*. An Arrhenius analysis of the degradation and regeneration rates, extracted from the proposed model, determines activation energies of 1.08 ± 0.05 eV for the degradation process and 1.11 ± 0.04 eV for the regeneration one. An improvement of the minority carrier effective lifetime of up to 40% is observed after a long dark anneal process. This improvement is associated with enhancement of both the bulk and surface passivation. Temperature- and injection-dependent lifetime spectroscopy measurements indicate that the recombination parameters of the associated defect causing the degradation in the dark are similar to those determined for the CID-related defect; therefore, it seems both defects have a similar nature.

In the second part of the study, the effect of the illumination intensity at *room temperature* on the degradation/regeneration is studied. Surprisingly, an improvement in the effective lifetime is found, followed by a very slow degradation. The proposed model is found to be suitable to fit these measurements. The extracted rates suggest that the observed behavior is due to a regeneration that is much faster than the degradation.

The reported findings provide new insights into CID in *p*-type mc-Si that will help improve understanding and assist in developing mitigation solutions.

1. Introduction

Degradation of multicrystalline silicon (mc-Si) solar cells under illumination and elevated temperatures was first reported by Ramspeck et al. [1]. Similar degradation was later observed by Kersten et al. [2] who named it light- and elevated temperature-induced degradation (LeTID). Differences in degradation kinetics between open- and short-circuit conditions [2] led some research groups to refer it as carried-induced degradation (CID) [3,4]; this is the term that will be used in this study. CID/LeTID is currently receiving large attention, as it can lead to efficiency losses of up to 16% (relative) of the passivated emitter and rear cell (PERC) fabricated on mc-Si substrates [5].

It is widely accepted that CID is caused by a bulk-related defect (or defects). Nakayashiki et al. [6] measured a significant reduction of the *bulk* minority carrier lifetime after light soaking at elevated temperature. Vargas et al. [7] reported no degradation of the surface passivation quality when monitoring it during CID. Additional evidence of a bulk defect was presented by Padmanabhan et al. [8] as degradation and regeneration were observed on PERC and aluminum back surface field (Al-BSF) cells. Despite the increased research interest in the last years, the bulk defect responsible for CID has not been yet identified. Ramspeck et al. [1] discarded boron-oxygen (B-O) complex as the cause for the degradation, as CID was detected also in gallium (Ga) doped wafers. It is also known that the concentration of interstitial oxygen is considerably lower in mc-Si wafers compare to Czochralski (Cz) wafers [9]. Moreover, the formation rates of CID are much slower than those reported for B-O [1]. They are also slower than the dissociation rate of the iron-boron (Fe-B) pairs. Inglese *et al.* suggested a possible involvement of copper (Cu) [10]. However, it seems this involvement is not supported by a recent study of Schmid et al. [11], who

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measured CID rates of mc-Si wafers contaminated with Cu and other metal impurities.

It is known that CID has a strong dependence on the firing conditions [7,12,13]. CID is less severe in samples fired at low peak temperature (< 600 °C) and it is not present in non-fired samples [12]. In addition, Zuschlag et al. [14] reported different CID behaviors after diffusion and gettering steps, while Chan et al. [15] reported modulation of the CID behavior using an initial dark anneal (DA). In general, it appears that CID has a strong dependence on the thermal history of the mc-Si wafers and cells. Due to the fact that hydrogenated surface passivation layers and the firing step are required for the formation of CID, hydrogen has been suggested as a potential candidate [15–17]. Our recent study using dielectrics containing different hydrogen concentrations provided the first ever experimental support for this suggestion [7]. Involvement of hydrogen in the regeneration was also proposed by Bredemeier et al. [18]; based on their model for CID whereby the regeneration is attributed to the diffusion of the CID defect to the wafer surface, they investigated the CID dependence on wafer thickness and found that the apparent diffusion coefficient of the CID defect was similar to that of hydrogen [18].

Lifetime spectroscopy techniques have been applied to identify the CID-related defect [6,13,19,20]. Based on injection dependent lifetime spectroscopy (IDLS), Nakayashiki et al. [6] determined a capture cross-section ratio [$k = \sigma_n/\sigma_h$; where $\sigma_{n(h)}$ is the electron (hole) capture cross section] value of 28.5 based on lifetime measurements at room temperature (RT) and assuming a mid-gap defect. Bredemeier et al. [13] also used IDLS at RT to determine $k = 20 \pm 7$ (assuming a mid-gap defect). Morishige and Jensen et al. [19] reported a defect energy level within the wide range -0.27 eV < $E_t - E_i$ < 0.13 eV and 26 < k < 36 using a sensitivity analysis of the defect parameters surface solution (DPSS, [21]) curves for IDLS measurements at RT. Tungsten (W), titanium (Ti) and molybdenum (Mo) were suggested as possible candidates. Recently, Vargas and Zhu et al. [20] used temperature- and injection-dependent lifetime spectroscopy (TIDLS) to determine a narrower range of E_t - E_i = (-0.32 ± 0.05) eV with k of (56 ± 23) or E_i – E_t = (0.21 ± 0.05) eV with k = (49 ± 21). Unfortunately, the reported uncertainty associated with the recombination parameters of metal impurities is quite wide and therefore several defects can still be considered as candidates. Of course, there is the possibility of a new defect that has not been studied previously.

Recently, Chan *et al.* [15] reported degradation of mc-Si cells due to DA at moderate temperatures. This work was later extended by Fung et al. [22] confirming degradation due to DA and by Chen et al. [17] who reported similar degradation and lifetime recovery due to DA of B-doped Cz and mc-Si wafers. These studies are the first to show CID without optical or electrical carrier injection. Fung et al. [22] proposed that during DA defect precursors move into the Si bulk from a reservoir. The subsequent DA and light soaking deplete that reservoir and leads to a lower CID extent after a few degradation-regeneration cycles [22]. Based on IDLS analysis, Chen et al. [17] found similar recombination parameters for the CID and DA associated defect in mc-Si; in addition, they found a similar firing dependence of the degradation under illuminated and DA [17]; therefore, they concluded that both defects are likely to have the same nature.

A few approaches have been used in order to determine the time evolution of CID [4,23]. Kwapil et al. [4] found that the degradation rate is proportional to the excess minority carrier concentration (Δn), suggesting that electrons are associated with the degradation. They used a single exponential function to extract the rates. However, they also suggested an improved fit using two exponential functions to describe slow and fast forming defects, although they also mentioned that the degradation and regeneration can happen simultaneously [4]. Bredemeier et al. [23] used illumination along with thermal treatment (75–120 °C) to degrade the samples. They considered only the degradation part of the kinetics curve to determine the presence of two defects (fast and slow). Using an Arrhenius analysis they extracted the activation energies of both (E_{fast} = 0.89 ± 0.04 eV and E_{slow} = 0.93 ± 0.06 eV [23]).

In this contribution, we investigate the temperature dependence, as well as the time evolution, of the degradation and regeneration of *p*-type mc-Si wafers under DA. We suggest that the degradation and regeneration are happening simultaneously, and propose a model to support this suggestion. TIDLS measurements are used in this work to estimate the recombination parameters of the involved defects. It was confirmed that the DA-related defect is identical to the CID-related defect. Finally, we investigate the dependency of CID on the light intensity at RT.

2. Sample preparation and measurement procedure

Ten six-inch neighboring high-performance boron-doped mc-Si wafers from a central brick with a thickness of 0.0192 ± 0.0003 cm and resistivity 1.70 ± 0.02 Ω cm [bulk duping N_A = (8.6 ± 0.1) × 10^{15} cm^{-3}] were used in this study. Symmetrical lifetime structures were prepared using the front PERC scheme [diffused layer passivated with silicon nitride (SiN_x)]: RCA (Radio Corporation of America) cleaning, 60 ± 3 Ω/□ phosphorous diffusion (both sides; carried out in a Tempress $POCl_3$ tube), hydrofluoric (HF) dip to remove the phosphosilicate glass, a second RCA clean before SiN_x deposition onto both sides using a Meyer Burger MAiA plasma enhanced chemical vapour deposition (PECVD) system. The obtained 75 nm SiN_x layer (refractive index 2.08 at 630 nm) [24] was then fired in a belt furnace at a sample peak temperature of 800 °C.

The six-inch wafers were then laser cleaved into tokens of 3.9 cm × 3.9 cm. The tokens were then split into three groups of sister tokens. **Group I** was dark-annealed using a hotplate (IKA c-mag HS 10) at eight *wafer* temperatures (138 °C, 160 °C, 176 °C, 203 °C, 228 °C, 254 °C, 275 °C and 300 °C), as measured by a *k*-type thermocouple in direct contact with a similar token. **Group II** was used for TIDLS measurements. The wafers were measured before the process and at the most degraded stage, based on the results of Group I. We measured wafers dark annealed at 138 °C, 160 °C, and 176 °C. Wafers of **Group III** were illuminated at RT (20–25 °C) at six light intensities [3 kW/m^2 (halogen lamps), 5 kW/m^2, 10 kW/m^2, 15 kW/m^2, 30 kW/m^2 and 45 kW/m^2 (all using a 938 nm laser – see below)]. In order to keep the wafers at RT during the illumination, a cooled stage was used (5310 Arroyo Instruments). The sample's temperature under illumination was measured in situ using an infrared thermometer (PC301HT-0, Calex). One token from each group was used as a baseline undergoing the laser-accelerated degradation of Payne *et al.* [3]. This process was done at temperature of 140 °C using a 45 kW/m^2 laser.

As Fe was detected in the samples, they were kept in the dark for at least six hours, much longer than the expected association time of Fe-B pairs in this substrate (0.8 h) [25]. The effective lifetime measurements were then taken using a photoconductance (PC) based lifetime tester (WCT-120 from Sinton instruments, actual sample temperature of 30 °C) using the generalized analysis method [26]. These measurements were followed by photoluminescence (PL) images (LIS-R1 from BT Imaging) using an 810 nm laser with a photon flux of 2.55 × 10^{17} cm^{-2} s^{-1} and an exposure time of 0.3 s.

The TIDLS measurements were made with a customized lifetime tester at UNSW, whose capabilities include PC and PL measurements, and a wide range of measurement temperatures (-190 to 400 °C) [20]. The measurements were done at sample temperatures of −22 °C, 0, 2 °C, 24 °C, 48 °C and 73 °C, before and after the respective DA treatment (wafers Group II). The Shockley-Read-Hall (SRH) lifetime [27,28] of the defect associated with the DA degradation ($\tau_{SRH,DA}$) was calculated as the harmonic difference between the non-degraded (τ_{fire}) and degraded (τ_{deg}) states effective lifetimes:

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