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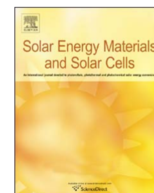

Light and elevated temperature induced degradation in p-type and n-type cast-grown multicrystalline and mono-like silicon

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ABSTRACT

We compare light induced degradation behaviours in lifetime samples and fully fabricated solar cells made from p-type boron-doped high performance multicrystalline silicon, p-type boron-doped mono-like silicon, n-type phosphorus-doped high performance multicrystalline silicon and p-type boron-doped Czochralski-grown silicon. Our results confirm that the degradation in multicrystalline silicon is triggered by the rapid cooling after the firing process. All cast-grown silicon samples subjected to fast cooling show lifetime reduction after light soaking. Interestingly, the degradation rate in n-type multicrystalline silicon is found to be orders of magnitude slower than in p-type multicrystalline silicon, suggesting that the defect formation mechanism could be affected by the positions of the quasi fermi levels.

1. Introduction

Solar cells made from multicrystalline silicon (mc-Si) suffer from an unexpectedly strong light induced degradation (LID) phenomenon that cannot be attributed to the boron-oxygen (BO) complex [1–3] commonly observed in p-type boron-doped Czochralski-grown silicon (Cz-Si). This degradation effect is commonly referred as light and elevated temperature induced degradation (LeTID), since the degradation measurements are typically performed at a higher temperature to accelerate the reaction, which otherwise occurs too slowly to be measured within a reasonable time scale at room temperature. Solar cells based on the passivated emitter and rear cell (PERC) structure are reported to be particularly affected by this degradation [4–8]. A performance loss of up to 7% at the module level is estimated within the first 3 years after installation [9].

The root cause for the degradation remains unclear to date. Studies have linked LeTID to the high temperature processing steps in solar cell fabrication [7,10–14]. Bredemeier et al. [12] compared mc-Si wafers fired at 900°C and 650°C, and only observed severe lifetime degradation in wafers fired at 900°C. Chan et al. [10] suggested that substantial LeTID can only be triggered if the peak firing temperature exceeds 700 °C, and can be largely reduced by incorporating an additional firing step at a reduced temperature afterwards. Eberle et al. [14] showed that wafers that were subjected to a fast firing process exhibit significantly stronger degradation than wafers subjected to the same peak firing temperature, but with slower heating and cooling rates. Zuschlag et al. [13] demonstrated that non-gettered wafers are more sensitive to LeTID compared to gettered samples. Moreover, it has been found that the rate and extent of the degradation depends not only on temperature [15], but also on the carrier injection level [16], which is influenced by the operating conditions [17,18] (e.g. open-circuit, short-circuit and maximum power point) and the illumination intensity [15,19]. In addition, recent works [20] have reported that the degradation can also be induced by dark annealing at elevated temperature, even without the presence of light.

Various solutions have been proposed to mitigate LeTID. One strategy is to prevent LeTID by adapting solar cell fabrication processes, such as applying a lower peak firing temperature [7,10,12], changing the firing profile [10,14], or rearranging the processing sequence [17,18]. These methods are effective in avoiding LeTID, but often require significant modifications in the processing which may not be feasible for industrial production. Another strategy is to erase the impact of LeTID by activating and accelerating the regeneration process that occurs after the degradation, through annealing the solar cells at higher temperature with stronger illumination [10,19,21,22], or under biased conditions [17,18]. These methods have proven to be effective in passivating LID caused by BO defects [23], but may not be so successfully applied on LeTID, due to its slow reaction rate and the uncertain long-term stability of the regenerated cells.

In addition to p-type mc-Si, some very recent works have observed

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similar degradation activities in p-type boron-doped Cz-Si [20,24] and float-zone Si [25–27] when illuminated at elevated temperature. In this paper, we will compare the degradation kinetics on three types of cast-grown Si materials, namely p-type boron-doped high performance (HP) mc-Si, p-type boron-doped mono-like Si and n-type phosphorus-doped HP mc-Si. Also grown by directional solidification, mono-like Si contains similar amounts of metal impurities compared to mc-Si, but features a distinct crystallographic structure [28,29], making it a suitable material for investigating the possible roles of metal impurities, grain boundaries and crystal dislocations in LeTID. On the other hand, n-type mc-Si does not contain boron, hence is not affected by BO defects and iron-boron (Fe-B) pairing reactions [30]. Furthermore, the use of n-type material may reveal any influence of the position of the quasi fermi levels on LeTID, which may in turn provide additional insights into the origins of the defects responsible for the degradation.

2. Experimental methods

Cast-grown wafers studied in this work were cut from the middle section of a central brick of a p-type boron-doped HP mc-Si ingot, an n-type phosphorus-doped HP mc-Si ingot and a p-type boron-doped mono-like Si ingot respectively. All ingots were cast in industrial G6 crucibles. The p-type and n-type HP mc-Si ingot were grown by the same manufacturer, whereas the mono-like Si ingot was produced by a second manufacturer. P-type boron-doped Cz-Si wafers were also included in the study as a reference. All wafers were around 200μm thick before processing. Table 1 summarises the resistivity and the interstitial oxygen concentration measured with Fourier Transform Infrared Spectroscopy (FTIR) for the studied wafers.

The wafers were processed into lifetime test structures, based on a PERC fabrication process without the metallisation step, in an industrial production line. The cell process involves texturing, $POCl_3$ diffusion, rear-side etch and surface passivation. The p-type samples feature plasma enhanced chemical vapour deposition (PECVD) SiN_x films on the front surfaces, and Al_2O_3/SiN_x stacks on the rear surfaces. The n-type samples feature PECVD SiN_x films on both front and rear surfaces. The samples were then divided into four groups and fired under different conditions. Wafers from group A were non-fired control samples. Wafers from group B were fired in an industrial conveyor-belt furnace in a cell production line, with a peak temperature of approximately 700℃. Wafers from group C and D were annealed in a rapid thermal processing (RTP) furnace at an actual temperature of 700℃ for 5 s (as measured by a thermocouple attached to the sample), followed by different ramp-down rates (20℃/s for the slow-cooled samples and $65-85$℃/s for the fast-cooled samples). The reported cooling rate is the average cooling rate between 700℃ and 400℃. An identical ramp-up rate (20℃/s) was applied to all RTP-processed wafers.

Additional samples were prepared to evaluate the influence of surface passivating films on the degradation properties. The samples received similar treatments as the n-type samples mentioned above. After surface passivation, all wafers were fired in an industrial conveyor-belt furnace, then had the dielectric films and the n + layers removed via HF dip. Afterwards, the wafers were chemically polished, separated into two series, and re-coated with two different dielectric films for surface passivation. Wafers from the first series were coated with SiN_x deposited using a Roth & Rau AK400 PECVD system. The wafers were heated with a ramp-up rate of around 10℃/min from 150℃ to 300℃ where the temperature was held stable for 23 min for films deposition, before cooling down at around 7.5℃/min and unloading at 150℃. Wafers from the second series were coated with a stack of Al_2O_3 deposited by plasma-assisted atomic layer deposition (ALD) and SiN_x deposited using an Oxford PlasmaLab PECVD system. The Al_2O_3 films were deposited at 175℃ for around 40 min, whereas the SiN_x films were deposited at 400℃ for around 8 min. After film deposition, the wafers were annealed in a nitrogen ambient at 425℃ for 15 min to activate the surface passivation of the Al_2O_3 films. Both selected dielectric films provide excellent surface passivation with S_{eff} below 10cm/s, confirmed with monocrystalline silicon control wafers.

Degradation was performed on a hotplate under illumination with a halogen lamp at around 2 sun light intensity. Rather than using 1 sun condition, we chose to use a slightly higher light intensity to accelerate the degradation [19]. The wafers were illuminated at 80℃ and 145℃ respectively. Before the degradation, the samples were annealed in the dark at 200℃ for 15 min. The effective carrier lifetimes were measured at defined time steps during the degradation, using the quasi-steady-state photoconductance (QSSPC) technique [31] and photoluminescence (PL) imaging [32].

Moreover, the work also includes several p-type PERC solar cells made from Cz-Si, HP mc-Si and mono-like Si to show the detrimental impact of LeTID on finished cells. The solar cells were randomly selected from an industrial production line. The wafers used were sourced from the same suppliers, but taken from different ingots than the lifetime samples described above. The degradation treatment was carried out in a light-soaking chamber at around 65℃ for 5 h under an irradiance level of 1 sun. The cell efficiency was measured before and after the degradation, using a solar simulator. Note the different degradation conditions used in the finished solar cells and the lifetime test samples mentioned above, as the degradations were performed with different equipment setups.

Table 1
Properties of materials studied in this work.

Material	Dopant	Resistivity (Ω cm)	$[O_i](cm^{-3})$
p-type HP mc-Si	Boron	1.7	1.7×10^{17}
n-type HP mc-Si	Phosphorus	2.1	NA
p-type mono-like Si	Boron	1.4	2.3×10^{17}
p-type Cz-Si	Boron	1.6	5.6×10^{17}

3. Results

Table 2 shows the degradation in the studied p-type PERC solar cells after 5 h of light soaking at 65℃ under an irradiance level of 1 sun. Note that Table 2 only provides an illustration of the degradation trends, as the degradation maximum has not been achieved given the short illumination time. Nevertheless, the results clearly demonstrate that all three types of solar cells exhibit degradation behaviour under illumination. A relative degradation of 4.3% and 4.6% was observed on the HP mc-Si and Cz-Si PERC solar cells after light soaking. Surprisingly, the degradation was most severe on the mono-like Si PERC solar cells, with an average relative degradation of 9.1%. This is contrary to a previous study by Ramspeck et al. [4] who observed a smaller degradation on mono-like Si PERC solar cells compared to conventional mc-Si PERC solar cells. A possible explanation is that the two materials (mono-like Si and HP mc-Si) contain different impurity concentrations as they were grown by different manufacturers. However, we have observed a similar behaviour on solar cells made from HP mc-Si and mono-like Si materials grown by the same manufacturer (measurements not presented here). In any case, our results show that the degradation in

Table 2
Efficiency variation in p-type boron-doped PERC solar cells after 5 h of light soaking at *65℃* under an irradiance level of 1 sun.

Material	Number of cells	Avg. initial efficiency	Avg. final efficiency	Relative degradation
p-type HP mc-Si	4	19.0%	18.2%	4.3%
p-type mono-like Si	4	19.7%	17.9%	9.1%
p-type Cz-Si	5	20.9%	19.9%	4.6%

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