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Correlation of the LeTID amplitude to the Aluminium bulk concentration and Oxygen precipitation in PERC solar cells

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ABSTRACT

We performed an extensive study of light induced degradation experiments in PERC solar cells made of Boron doped Cz Silicon material from several experimental crystals. Strong LeTID (Light and Elevated Temperature Induced Degradation) amplitudes were found in cells originating from the top and tail part of the crystals. A statistical analysis reveals a strong correlation to the bulk concentration of Aluminium in cells originating from wafers close to the tail. Close to the top, the LeTID effect is strongly enhanced whenever Oxygen precipitation occurs in the cell process.

1. Introduction

In recent years, Silicon solar cell efficiency in industrial processes has increased to new record levels, exceeding 22% [1,2]. This was made possible by a switch from the previous standard technology using an Aluminium Back Surface Field (Al-BSF) process to the so-called PERC technology (Passivated Emitter and Rear Solar Cell). In the Al-BSF process, recombination at the interface between Silicon bulk and the rear metallization was the dominant loss mechanism. PERC solar cells, on the other hand, are now limited to a larger extent by the electrical quality of the front (emitter and passivation) and by recombination processes in the Silicon bulk. Recombination active defects, either originating from crystal growth, introduced during cell processing or being activated by illumination, therefore cause a stronger relative decrease in cell efficiency than in Al-BSF cells.

Light induced degradation (LID) in Silicon solar cells was already observed in the 1970s [3]. Since a correlation of this effect to both the Boron and the Oxygen concentration was observed [4], the defect causing this degradation was called “Boron-Oxygen defect”, even though the exact defect configuration has not been determined to date. In order to distinguish this kind of degradation from the other ones discussed in the following, we use the term “B-O LID” for this effect. Later, Möller and Lauer suggested that Oxygen was not directly involved in the “Boron-Oxygen defect”. They suggested an “A_{Si}-Si_i” configuration, where “A” stands for the possible acceptors Aluminium, Boron, Gallium, and Indium [5,6]. This complex defect consists of an acceptor atom on a substitutional Silicon site, accompanied by a displaced Silicon atom on a nearby interstitial site.

When the PERC process sequence started to become industrially feasible, Ramspeck et al. observed an unexpectedly high degradation upon illumination at moderately increased temperature (75 °C) [7]. This effect was particularly strong in cells made of multicrystalline or mono-like (QuasiMono) wafer material. The Oxygen concentration in these wafer types is considerably lower than in Czochralski (Cz) material, which made it unlikely that this degradation was the same as the B-O LID described above. Due to its particular features, and in order to distinguish it from the B-O LID effect, Kersten et al. introduced the name LeTID (Light and elevated Temperature Induced Degradation) for this phenomenon [8]. It was originally believed that LeTID only occurs in multicrystalline material. Later it was detected also in solar cells made from Cz crystals [9]. It is of major importance to understand the origin of this phenomenon, since it is, in some respects, more severe than the well-known B-O LID. In particular, its regeneration behavior is more unfavorable.

In order to identify the root cause for the LeTID phenomenon, both experimental and theoretical investigations have been published. It was shown that LeTID in multicrystalline material only occurs when a passivation layer is present on at least one wafer surface during the fast firing step, which is necessary for contact formation to the metallization [10]. Vargas et al. interpreted this finding as related to the amount of Hydrogen released from the passivation layers into the wafer bulk during the fast firing [11]. By using both injection dependent and

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temperature dependent lifetime spectroscopy, Morishige et al. could narrow down the possible values for the relevant defect parameters after degradation in LeTID dominated multicrystalline material. By comparing these to literature values, they suggested that LeTID may be related to the presence of Tungsten [12]. Later on, Niewelt et al. found "denuded zones" of reduced LeTID amplitude in the vicinity of grain boundaries in multicrystalline material. These denuded zones are assumed to originate from a gettering effect of the grain boundaries on one of the elements involved in the defect underlying the LeTID effect. From the width of the denuded zone, they could draw conclusions about possible candidates, since the solubilities and diffusivities of most of the relevant metallic impurities at the process temperatures during cell processing are known. Based on this, it was suggested that the LeTID phenomenon may be related to Cobalt contamination [13].

It has been shown by several groups that the amount of degradation due to the LeTID phenomenon can be influenced by variations in cell processing, in particular by optimization of the fast firing profile [14]. In our screening of solar cells produced from a large number of different experimental B-doped Cz crystals, we find strongly varying LeTID amplitudes for identical cell processing details, in particular when fired using identical profiles. This implies that the origin of the LeTID phenomenon lies in properties of the Cz material itself. No attempt was made to vary the Hydrogen content in our solar cells. All cells were coated with dielectric layers on both sides using standard process parameters in all cases. We can, thus, assume that the Hydrogen content is comparable in all experiments. No conclusions about the involvement of Hydrogen in formation of the LeTID phenomenon are possible based on our studies.

The price for the raw Silicon wafer constitutes a significant share of the final price for a PV module. In a highly competitive environment, all processes have to be continuously optimized concerning their costs. Before introducing cheaper components (e.g. Silicon feed stock, graphite parts in Czochralski furnaces, crucibles, …) into production, the impact of this process change on wafer quality has to be evaluated. For this purpose, it is very important to quantify critical concentrations of relevant impurity elements, which can be tolerated. Another important cost saving measure is to pull multiple crystals out of the same crucible by recharging after each pull. Up to three crystals were pulled consecutively in our experimental program and evaluated concerning their efficiency potential and their degradation behavior.

In previous experiments, we repeatedly and reproducibly found a systematic variation of the LeTID amplitude along the crystal length. Since the wafers were randomized prior to and during cell processing, a systematic influence of the cell processing, leading to the observed behavior, could be ruled out. The LeTID defect, or one of its constituents or precursors, has to consist of defects already present in the grown Cz crystal.

The major defects in electronic grade Cz material are related to Oxygen and to crystal defects originating from a vacancy or self-interstitial supersaturation. Whether a Cz crystal contains mainly vacancies or self-interstitials, is determined by the value of the so-called Voronkov coefficient v/G, where v is the pulling speed and G the thermal gradient across the growth front [15]. The Oxygen content can be altered by measures like varying the Argon flow rate, the crystal rotation or the process pressure. Systematically changing these parameters, we assumed to be able to influence the LeTID behavior.

Alternatively, we suspected that some kind of impurity is responsible for LeTID. This was based on the observation of increasing LeTID amplitude towards the tail and from 1st to 3rd pull (see below). It is also in line with part of the literature cited above. In order to test this hypothesis, we varied the feedstock, e.g. by increasing the remelt fraction or using 100% prime poly material.

2. Experimental details

2.1. Sample preparation

In our experimental program we grew Boron-doped Cz crystals with strongly varying properties. The more than 40 growth runs can roughly be grouped as aiming at:

(i) Varying the concentration of the intrinsic defects (Silicon interstitials or vacancies) in a systematic way;
(ii) Reducing the Oxygen concentration;
(iii) Reducing the concentration of relevant metallic contaminations.

In (i) we varied both the pulling speed and the temperature gradient at the growth front (aiming at varying Voronkov coefficients, thus introducing different amounts of Silicon interstitials or vacancies, respectively [15]). Examples for measures to influence the Oxygen concentration (ii) are: Increased gas flow rate, reduced process pressure or changes in the hot-zone design. For (iii), we compared crystals grown from 100% prime poly feedstock to different feedstock compositions. In addition, critical components in the Cz furnaces were exchanged, in particular we used crucibles from different vendors and varying quality. Up to three crystals were pulled consecutively from the same crucible.

We measured the concentration of relevant impurities at several positions in our crystals. Each complete crystal was cut into four sections with a length of typically 500 mm. The top-most section is called "A", the tail-most one "D". We cut thicker slices from the very top and very tail of the first and last section. The nomenclature is visualized in Fig. 1.

The resistivity of the samples was determined by the Four-Point-Probe technique; both initially and after an appropriate thermal donor anneal (720 °C, 120 s in an RTP furnace). The Oxygen and Carbon concentrations were obtained from Fourier Transform Infrared Spectroscopy (FTIR) measurements.

Metal impurity concentrations were determined using ICP-MS (Inductively Coupled Plasma Mass Spectroscopy). For this purpose, small pieces were cut from the thick slices close to the center position. They were carefully surface etched several times (total etch removal at least 10 µm) in order to remove possible surface contamination contributions. After that, the pieces of Silicon were completely dissolved in a gaseous HF/HNO_3-atmosphere in order to receive a matrix reduced residue, which is re-dissolved for ICP-MS measurement. In this technique, the measurement effort increases with every element which has to be screened. Based on the experience obtained in previous experiments we focused on the following elements: Fe, Cr, Ni, V (elements contained in stainless steel parts), Cu, Ti, Zn, Al. In some cases, also the concentrations of Mo, W, Pb and Co were determined. However, for these elements the available data is not sufficient for a statistical analysis.

The entire crystals (except the thick slices) were wafered in an industrial wafering process. They received a special laser marking, coding their vertical position in the crystal. Then they were processed into Cz-PERC cells using an industrial cell process. Typically, we achieved cell

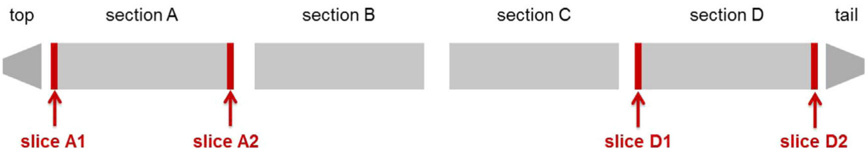

Fig. 1. Naming of the crystal sections and position of the thick slices used for determination of the impurity concentrations.