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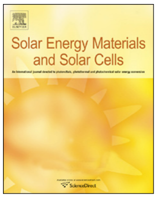

Efficiency limiting crystal defects in monocrystalline silicon and their characterization in production

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ABSTRACT

Wafers and thicker slices of an entire n-type monocrystalline silicon ingot were studied using production-compatible electrical and optical characterization techniques. We investigated the capability of these techniques to detect efficiency limiting factors in the early phase of solar cell manufacturing. In addition to the standard characterization methods and parameters - carrier lifetime, resistivity, FTIR, photoluminescence (PL) - the OxyMap technique was used to evaluate the thermal history of the wafers, while the distribution of Bulk Micro Defects (BMD) was measured using Light Scattering Tomography (LST). PERT cells and samples with amorphous silicon surface passivation – deposited at low temperature – were produced from neighboring wafers to correlate silicon properties and solar cell efficiency results.

An interesting indirect correlation was found between “as-grown” lifetime and cell performance, as both are influenced by the thermal history of the wafer.

We also observed a very strong correlation between BMD position, measured by LST on as-grown samples, and defective areas on PERT cells localized by PL measurements. The LST measurements on heat treated samples (simulating the PERT cell process) showed the growth of BMDs in low efficiency areas. It indicates that the detection of harmful defects is possible even in the as-grown material using LST technique.

1. Introduction

Modern n-type silicon cell structures show the highest stabilized efficiency in mass production, which is around 22–22.5% in today's state-of-the-art production lines. A continuously increasing market share of both homo- and heterojunction n-type cell concepts is predicted [1]. To achieve the expected efficiency improvement, recombination currents need to be further reduced in industrial scale. One key factor is the stable high-quality, high volume, cost-effective production of n-type Czochralski silicon (Cz-Si) ingots, which is supported by the generally less harmful nature of metallic impurities in n-type Si compared to p-type Si [2].

The higher crystal pulling speed – applied for the Cz-Si crystallization processes in PV industry – improves the yield of the ingot production. On the other hand, the Si ingots are grown in vacancy-rich regime [3], which can be the origin of defect generation. In addition to the formation of voids in the 1000–1100 °C temperature range during the cooling of the crystal, the formation of oxide precipitates is a significant mechanism at slightly lower temperatures [4] due to the high degree of the Oxygen supersaturation, which results in an increased total density of bulk micro defects (BMD).

Based on Voronkov's theory [5], the distribution of vacancies and Si self-interstitials are determined by the pulling conditions (v/G, where v denotes the pulling speed and G the axial temperature gradient near the crystallization front). However, the size and distribution of the grown-in BMDs is a function of the thermal history of the growing process [3,6] influenced by a several additional parameters, such as the thermo-mechanical stress during the crystallization, and concentration of dopants and other impurities (C, Ni, metallic impurities) [3,7,8].

For Cz-Si based solar cells, SiO_2 precipitation may cause a significant degradation in bulk carrier lifetime, which leads to a reduction in cell efficiency up to 4% absolute [9,10]. Therefore, it would be favorable to detect BMDs (or corresponding nuclei) – not yet being harmful but prone to growth during subsequent process – in early phase of the production. However, as it is shown in the well-known work of Haunschild et al. [11], such detection in as-cut wafers faces difficulties.

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Namely, the observed ring patterns in photoluminescence (PL) images – caused by the variation of effective doping level - does not necessarily reflect/indicate reduced carrier lifetime in the finished homojunction cell.

For the crystalline / hydrogenated amorphous silicon (c-Si/a-Si:H) heterojunction solar cells (HJT) – using only low temperature manufacturing process steps – the efficiency of the finished cells can be predicted from *as-grown* bulk carrier lifetime and the bulk resistivity [12,24]. In some particularly defective Cz-Si wafers however, the knowledge of the as-cut lifetime may not be enough to predict the cell efficiency due to the formation of a light-induced defect upon illumination of the cell [13].

So far, the manufacturing of all types of homojunction cell structures includes high temperature process steps in the 800–1000 °C temperature range. During the diffusion or annealing processes, the nuclei formed during the crystallization grow further resulting in larger BMDs. Such precipitation may reduce the carrier lifetime, and consequently degrade the cell efficiency. Under industrial Cz-Si pulling conditions, wafers from the upper tens of centimeters of the ingot at the seed part is exposed to this precipitation phenomenon [6,14] if the pulling process is not controlled carefully.

Since these efficiency-limiting defects are generated during solar cell processing, their inspection in the as-grown crystal is problematic even by measuring the bulk lifetime [8,14], as their nuclei may simply show no recombination-activity.

One possible solution for such inspection is to apply the relationship between the thermal history and the final cell efficiency. It is shown in [6] that high Thermal History Index (THI) measured using the "OxyMap" technique [15] predicts the appearance of the ring pattern defects which reduce cell efficiency if the interstitial oxygen concentration [O_i] is sufficiently high.

Carrier lifetime (LT) and especially photoluminescence (PL) measurement methods are known to be efficient techniques characterizing the electrical quality of the Si samples at every stage of the PV cell production chain [16–18]. Size and distribution of microdefects are mostly characterized by optical microscopy after chemical defect etching. In the semiconductor IC industry – where the BMD size and density distribution are also important material parameters – Light Scattering Tomography (LST) is a known and accepted characterization technique, which is mostly used to inspect the quality of the defect-free denuded zone at the wafer surface [19].

In this work, we investigate the capability of the LST technique to detect BMDs in thick slices from as-grown crystal and try to confirm their detrimental impact on the solar cells efficiency.

2. Experimental

2.1. Sample preparation

A 90 kg phosphorus-doped Cz-Si ingot was crystallized, with an average pulling speed of ~ 36 mm/h. After squaring, the ingots were cut into four bricks (B1-B4). For FTIR and BMD characterization, 1 mm thick slices were cut from the ends of each brick (see Fig. 1).

After performing the relevant brick-level characterization, the bricks were sliced into wafers using the diamond wire sawing technique. Neighboring wafers were used for as-cut wafer characterization, for symmetrical intrinsic /n-doped (i/n) a-Si:H passivation stacks [12] and to manufacture PERT (Passivated Emitter Rear Totally diffused) cells at CEA-INES (details and the process flow are described in [20]). Around 40 solar cells and 40–40 as-cut and passivated wafers were fabricated for the study. The scheme of the performed measurements is summarized in Fig. 2. After the initial BMD characterization performed on the thick slices by LST, the samples were heat treated in two steps intended to mimic the PERT processing (within the 800–1000 °C range) and re-measured thereafter.

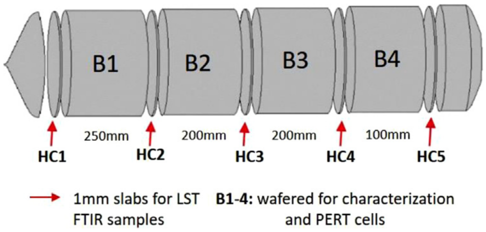

Fig. 1. Illustration of the ingot used for the study. 1 mm thick slices were cut from the end of each ingot part for FTIR and BMD characterization. Neighboring wafers from the four sections covering the entire length of the ingot were used for as-cut characterization, surface passivation and PERT cells.

2.2. Characterization techniques

In this work, the application of industrial-compatible, preferably non-contact measurement methods are studied. The characterization techniques and systems used for this study are listed below.

2.2.1. Resistivity

Resistivity (ρ) testing was performed on samples of all geometry types (bricks, thick slices, and as-cut wafers) using an eddy-current sensor. Resistivity measurement is available in different tools used for this study. The resistivity values determined by the different systems on all sample types were within 10% for the same part of the ingot. ρ values required for implied V_{oc}, (i-V_{oc}), [TD] and THI calculation were obtained using an OxyMap system from AET Solar Tech. Not to confuse the reader, we made the choice to only show results from the OxyMap system.

2.2.2. Carrier lifetime

Depending on the sample type and the distribution of the work for this study, carrier lifetime was tested using different measurement techniques and systems.

- Eddy-current PCD (e-PCD) technique [21] was applied for bulk lifetime measurements on the bricks using a Semilab WT-2000DI system.
- μ-PCD technique of Semilab WT-2000PVN system was used for effective lifetime (τ_{eff}) mapping in passivated samples.
- QSS- μPCD carrier lifetime measurements [22] were performed on the passivated wafers determine the carrier lifetime at given injection levels.
- τ_{eff} and i-V_{oc} values were obtained using the QSS-PC technique using a Sinton WCT-120 system at CEA- INES on PERT cell precursors (before metallization).

2.2.3. [TD], Thermal History Index

Determined by the OxyMap technique [15]. The method is based ρ measurements at as-grown state (ρ_1), after 450 °C TD generation annealing process (ρ_2), and finally after a TD killing annealing at 700 °C (ρ_3). Doping concentration, as-grown [TD], [O_i] and THI are calculated from these three ρ values. THI can be applied as an indicator of the cooling velocity of the material during the pulling process [6].

2.2.4. Quasi-Steady-State PL (QSS-PL) for passivated samples

PL images were captured using the on-the-fly PL imaging capability of the Semilab PLI-1001B system. For the proper in-line acquisition of PL images of passivated samples, the sample is illuminated in a wide stripe (perpendicular to transport direction), which ensures the steady-state conditions [17,18], while the PL photons are captures using a suitable CCD camera equipped with optimized optics.

Using similar optical arrangement, PL images of the bricks were recorded by a Semilab PLB-55 equipment.