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Investigation of iron contamination of seed crystals and its impact on lifetime distribution in Quasimono silicon ingots

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ABSTRACT

The use of seed plates during directional solidification (DS) of Quasimono silicon ingots causes additional yield losses compared to standard multi-crystalline ingots due to an increased area of low minority carrier lifetime ("red-zone") in the bottom region. This effect is attributed in literature mainly to iron impurities which are contaminating the seed crystal during heat up and afterwards the as-grown ingot during solidification. However, the contamination mechanisms itself are still not completely understood.

Therefore, in this work the seed contamination mechanisms by iron and their effect on the lifetime distribution in the bottom region of Quasimono silicon ingots were investigated. For this purpose special crystal growth experiments in a laboratory-scale DS furnace were carried out by using diffusion barriers at the crucible/seed and seed/melt interfaces in order to separate the different contamination paths. The results show that the iron diffusion path from the crucible into the seed plates plays an important role. But in addition to this it will be demonstrated that an even more important iron contamination path is by gas phase transport from furnace parts via the furnace atmosphere to the seed crystals.

1. Introduction

In recent years the Quasimono (QM) directional solidification (DS) technology was developed to produce high quality mono-crystalline silicon ingots for solar cell application by using seed crystals [1]. However, so far it is not clear, whether the QM technology can play a significant role in comparison to the Czochralski technique. The reason is that there are still several unsolved problems like the multi-crystalline grain growth in the border regions of the ingots [2] and the defect formation at the seed joints [3,4]. Both phenomena can drastically reduce the ingot yield of high quality mono-crystalline wafers resulting in higher production cost. Furthermore, there exist several unsolved problems concerning the expensive seed crystals which were normally cut from Czochralski-grown mono-crystals. One prominent question is the possibility of a multiple seed recycling for cost saving [5]. Another problem concerning the ingot yield is the fact, that the region of very low minority carrier lifetime (so called "red-zone") at the bottom of the silicon ingots is more extended in QM ingots in comparison to multi-crystalline ingots grown without seed crystals (see e.g. [6] and also Fig. 2 in this paper). Several groups [5–8] have shown experimentally and by calculations that this lifetime decrease (within the red-zone) is mainly caused by iron impurities. And it is claimed that the iron atoms are diffusing from the silica crucible into the silicon material. However, the exact mechanisms are still not completely understood. Especially for the occurrence of the increased iron concentration at or near the seeding interface are different models discussed in the literature. Gao et al. [7] have shown by simulations that the iron diffusion from the silicon melt into the seed crystal and the subsequent back-diffusion from the seed crystal into the grown crystal could be responsible for the increased iron concentration at the seeding interface. Yu et al. [8] claim the segregation-induced enrichment of iron in the melt in front of the growth interface in the initial stage of growth as the cause. Both mechanisms could be in principle possible, but were not confirmed by systematic experimental studies yet.

Therefore, the aim of this work is to evaluate the existing models for the lifetime and iron distribution in the bottom region of DS-grown QM silicon ingots by a precise study of the diffusion paths from the crucible and the silicon melt into the seed crystal. For that purpose special DS crystal growth experiments were carried out by using a newly developed iron diffusion barrier at the crucible bottom/seed crystal and seed crystal/feedstock interface, respectively (as sketched in Fig. 1 and described in Section 2).

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2. Solidification experiments and characterization

QM silicon ingots with ~100 mm in diameter, 60–70 mm length and a weight of about 1.2 kg were grown in a laboratory-scale VGF-furnace as described more in detail in an earlier publication [9]. The growth rate was about 1 cm/h and the growth interfaces were slightly concave. Solar grade silicon from Wacker was used as feedstock, contained in a cylindrical crucible made of fused silica and coated with silicon nitride. Mono-crystalline Czochralski seeds with 20 mm thickness and a diameter which is slightly smaller than the inner crucible diameter were placed at the crucible bottom. The resistivity of the Boron-doped seeds and the grown crystals was in the range of 2–1.5 Ω cm which corresponds to a boron concentration in the range of $7–9 \cdot 10^{15}$ at/cm³.

Some of the experiments were carried out by using a recently developed device called "diffusion barrier" which consists of a plate of a crystalline material [10] of 300 µm thickness. The diffusion barrier which effectively blocks the incoming iron was used in several experiments between the crucible bottom and seed crystal (see configuration D in Fig. 1). Additionally it was used in a few experiments between the seed crystal and the silicon feedstock (configuration E).

It should be remarked that some other research groups have already proposed various kinds of potential diffusion barriers to be used during growth of multi-crystalline silicon consisting of polysilazan [11,12] or barium oxide [12]. However, in both cases only a small reduction of the extension of the red-zone in the bottom region of the ingots was achieved. It will be shown in Section 3.2 that the new material used in this work is much more efficient in blocking the diffusion of iron.

Beside the QM silicon ingots also a multi-crystalline silicon ingot was grown by using a diffusion barrier located at the crucible bottom (configuration B). For comparison also QM and multi-crystalline reference crystals (configuration C and A, respectively) were grown without using any diffusion barrier.

The as-grown ingots were cut parallel to the growth direction to prepare wafers of 2 mm thickness from the center of the ingot. After mechanical polishing (1 µm) the minority carrier lifetime was measured by the microwave-detected photoconductance decay (µ-PCD) method. Due to the low lifetime range below 5 µs the measurements were done without any surface passivation. Also the distribution of interstitial iron (Fe_i) was determined by this method. The Fe_i concentration is calculated by the change in lifetime before and after illumination due to the dissociation of Fe–B pairs [13]. Additionally the total iron concentration (Fe) was locally measured at positions below and above the seeding interface by secondary ion mass spectroscopy (SIMS).

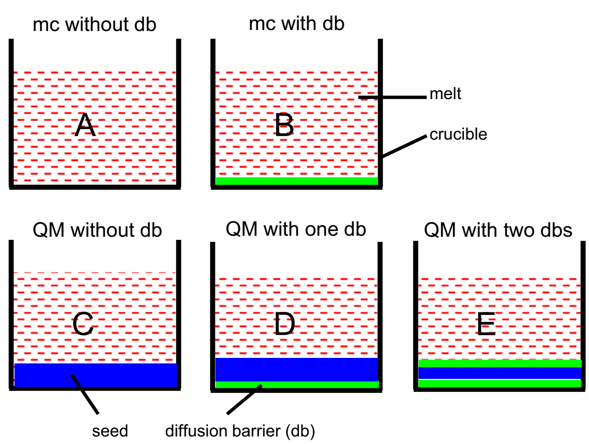

Fig. 1. Schematic representation of the DS growth configurations A–E used in the solidification experiments in this work: without (A, B) and with seeds (C–E); without (A, C) and with (B, D, E) diffusion barriers (db).

3. Lifetime and Fe_i distribution in the grown silicon ingots

3.1. Silicon ingots grown without diffusion barriers (reference experiments)

Fig. 2 shows the distribution of minority carrier lifetime of a "standard" (meaning without diffusion barrier) multi-crystalline silicon ingot (configuration A, Fig. 2a) and a standard QM silicon ingot (configuration C, Fig. 2b) on a wafer cut parallel to the growth direction. In both cases the well-known distribution of lifetime in directionally solidified silicon ingots appears. An area of high lifetime in the central volume of the crystals is completely surrounded by low lifetime regions, called "red-zone". Clearly the length of the red-zone at the side walls (mainly attributed to an out-diffusion of iron from the crucible walls) and at the top of the ingots (mainly attributed to a back-diffusion of segregated iron) are comparable for both ingots. But it is obvious that the length of the red-zone in the bottom region (depicted in Fig. 2a and b by the black arrows) is much larger in the QM silicon ingot (b) than in the multi-crystalline silicon ingot (a). Roughly there exists the following correlation between the length of the bottom red-zone in the QM ingot L_{QM} and in the multi-crystalline ingot L_{mc}: $L_{QM} \approx L_{mc} + d_{Seed}$ where d_{Seed} is the thickness of the remaining seed crystal

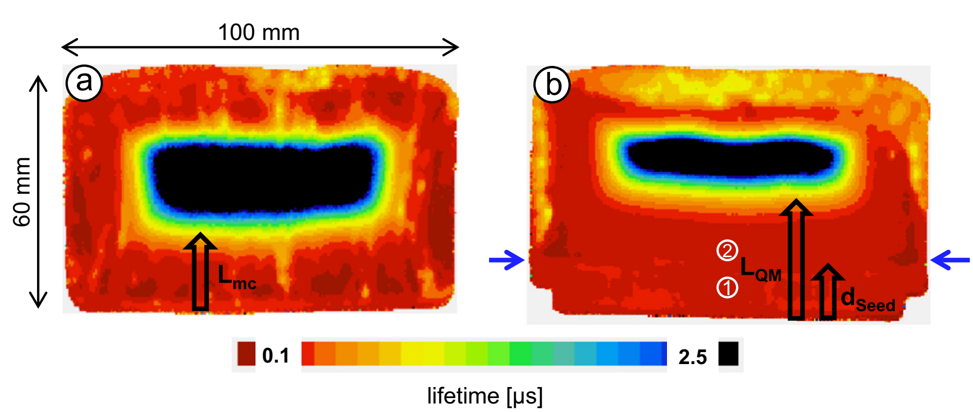

Fig. 2. Distribution of lifetime in a standard multi-crystalline silicon ingot without seed (a) and a QM silicon ingot with seed (b). The seeding interface is depicted by the small blue arrows. The encircled regions (1) and (2) are marking the areas where the total Fe concentration was determined by SIMS analysis to be (1) $7.5 \cdot 10^{13}$ at/cm³ and (2) $5.3 \cdot 10^{14}$ at/cm³. The length of the red-zone in the bottom region of both ingots is marked by black arrows. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)