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Influencing factors on the formation of the low minority carrier lifetime zone at the bottom of seed-assisted cast ingots

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The effects of height of remaining seed, seed type, and crucible purity on the length of the low minority carrier lifetime zone (i.e., red zone) at the bottom of seed-assisted cast ingots were investigated. The red zone length at the bottom is proportional to the height of the remaining seeds. Only very little difference in the length of the bottom red zone was found in the quasi-single-crystal silicon (QSC-Si) bricks between using normal single-crystal seeds and recycled seeds, while the use of particle seeds resulted in a longer bottom red zone compared with using block seeds. Furthermore, a high-purity crucible does not result in a significant reduction in the height of bottom red zone in the QSC-Si ingot, although it results in a much shorter bottom red zone in the conventional mc-Si ingot.

1. Introduction

Multi-crystalline silicon (mc-Si) ingots grown by unidirectional solidification are still the main silicon solar cells material because of the cost-efficiency, high throughput, and large-scale production of the unidirectional solidification process. However, conventional mc-Si has a much lower quality than Czochralski (CZ)-Si crystals because of non-uniform randomly oriented crystal grains and structural defects, which lead to a large difference in their cell conversion efficiencies. In recent years, the seed-assisted casting method has been developed, which uses a conventional directional solidification (DS) process with additional seed crystals placed on the bottom of the crucible. The seed-assisted casting method has emerged as a promising technique for growing quasi-single-crystal silicon (QSC-Si) in the photovoltaic (PV) industry [1–5]. It offers lower manufacturing cost and higher throughput for silicon wafers than the CZ method, and higher conversion efficiency for solar cells than the conventional DS method. In addition, uniform small grains and low dislocation density can be obtained in the high-performance mc-Si ingots produced using multi-crystalline silicon seeds, which results in a higher average solar cell conversion efficiency (about 0.5% in absolute value) than that of conventional silicon [6]. However, a longer low minority carrier lifetime zone exists at the bottom of the seed-assisted cast silicon ingot, which lowers the ingot yield and increases the cost of seed-assisted cast silicon products.

Among the key parameters that ultimately control the performance of a solar cell, minority carrier lifetime plays a crucial role [7], and the minority carrier lifetime depends on many factors, such as dislocation, iron impurities, and oxygen content [1,3,8–10]. The low minority carrier lifetime zones are commonly referred to as "red zones" in the PV industry. Owing to the seed crystals, the low minority carrier lifetime zones in the QSC-Si ingots show very different characteristics to mc-Si ingots. To enhance the competitiveness of seed-assisted cast silicon products, it is crucial to understand the formation cause of the red zones to increase the ingot yield. This subject has drawn much attention, and different models have been established to discuss the formation cause [11,12]. Studying the effects of the seeds and the crucible on the red zone is important to clarify the formation cause and find an effective way to reduce it.

In this study, we investigated the effects of the seeds and the crucible on the lifetime distribution in industrial-sized seed-assisted cast ingots, and the effect of the height of the remaining seeds on the red zone at the bottom in the QSC-Si ingot is discussed. To analyze the influence of seed type on the red zone, the lifetime mappings of the bricks using recycled and particle seeds are compared with normal ⟨100⟩-oriented single-crystal seeds. Furthermore, QSC-Si ingots were grown in crucibles with different purity, and a comparative analysis of the red zones is performed.

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2. Experiment and measurement

The QSC-Si ingot was cast in an industrial DS furnace [13]. A thermocouple (TC) was installed at the upper center of the heat exchange block to monitor the temperature at the crucible bottom. The volume of the quartz crucible used in the experiment was $840 \times 840 \times 420\ mm^3$ and coated with Si_3N_4 (Stack, M11 HP), then 440 kg silicon feedstock was loaded in it. Seed crystals were first paved across the entire bottom of the crucible. The thickness of the seed crystals was about 20 mm. Different types of seeds were used in our experiments. For comparative analysis, high-purity quartz crucibles with prefabricated coating were used and the conventional mc-Si ingots were also produced. The ingots were cast under the standard recipe for QSC-Si ingot and conventional mc-Si ingot used in the production line, and the average growth rate of the ingots was controlled about 1.2 cm/h. The grown ingots were cut into 25 bricks with a square cross-section of $156 \times 156\ mm^2$ by wire sawing, and then a minority carrier lifetime map of the as-cut bricks was obtained using microwave photoconductance decay (MW-PCD, Semilab WT2000).

3. Results and discussions

3.1. Effect of the height of remaining seeds

⟨100⟩-Oriented crystals cut from a CZ-Si ingot were used as seeds in the QSC-Si ingot casting. During the melting stage, the bottom of the seed was kept in the solid state, and then the liquid crystallized on the remaining seeds with the same orientation of ⟨100⟩. We randomly selected a group of QSC-Si ingots from the production line to analyze the bottom red zone which refers to the regions with lifetime lower than 2 μs for mappings by WT2000. The bottom red zone of every brick has been measured and the average length was defined as the red zone length value of the ingot. As shown in Fig. 1(a), the bottom red zone in the QSC-Si ingot is over 20 mm longer than that in the conventional mc-Si ingot. In this figure, the dotted lines represent the average values, and the result for the conventional mc-Si ingot is the statistical average of hundreds of ingots in the production line.

A longer bottom red zone in the QSC-Si ingot will decrease the yield of the ingot, weakening its competitiveness with the mc-Si ingot. However, the formation mechanism is still unclear. Obviously, it takes longer time at high temperature in the casting process for QSC-Si ingots because of seed preservation, providing more time for the impurities diffusing from the crucible, which would contribute to the formation of a longer bottom red zone in the QSC-Si ingot. But the resulting diffusion depth from the crucible bottom should not achieve that length of more than 50 mm.

In this aspect, different models have been proposed to discuss the formation cause recently. According to the model established by Gao et al. [11], the longer bottom red zone in the QSC-Si ingot could be caused by the back-diffusion of impurities from silicon melt into the seed at the seed preservation stage before crystal growth, while Yu et al. [12] pointed out that it mainly resulted from the diffusion of iron into the silicon bulk from the iron-rich layer at the initial stage of the crystallization process. The iron-rich layer was crystallized from the transient layer at the solid–liquid interface due to a rapid elevated growth rate, where most iron atoms remained. Comparing the diffusion sources in the two models, the impurity concentration in the iron-rich layer is much higher than that in the silicon melt, thus resulting in more remarkable influence on the concentration in the crystal. So the latter model is likely more feasible for the explanation of the significant longer bottom red zone in the QSC-Si ingot. However,

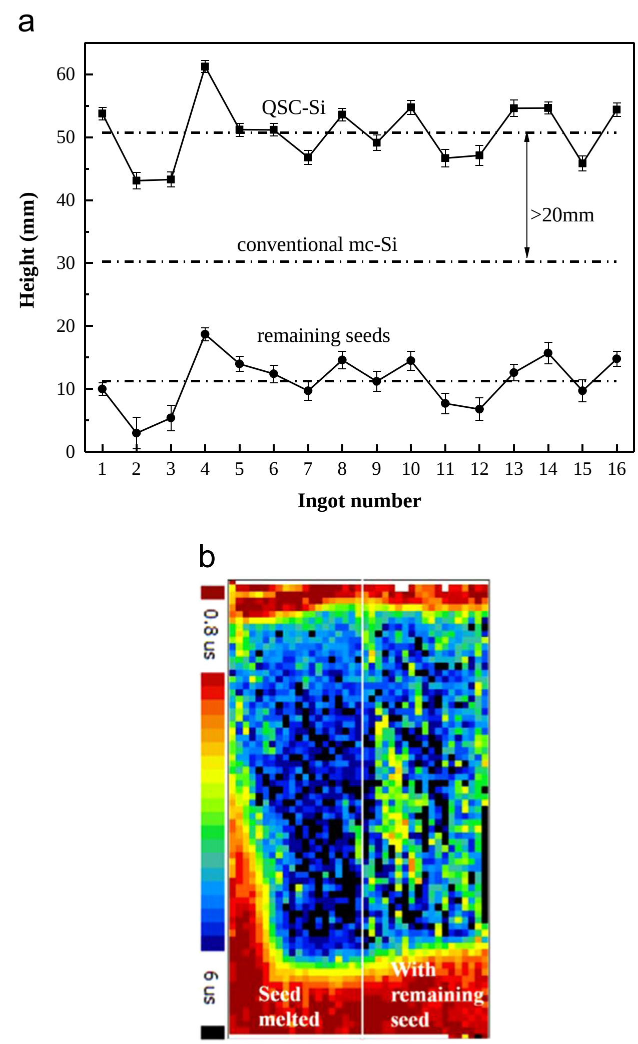

Fig. 1. (a) Length of red zones at the bottom and height of remaining seed crystals in different ingots. (b) Minority carrier lifetime map of a corner brick in which the seed crystal was partly melted.

the existence of solid seeds at the crucible bottom makes the formation mechanism of the bottom red zone more complicated. The longer bottom red zone in the QSC-Si ingot may be a result of manifold factors. A combination of the models proposed by Gao et al. [11] and Yu et al. [12] may give a better explanation of what we observed in our experiments which is to be discussed in more detail in the followed sections.

Fig. 1(a) also shows the relationship between the length of the red zone at the bottom and the height of the remaining seeds. It was found that the length of the red zone was proportional to the height of the remaining seeds. Fig. 1(b) shows the minority carrier lifetime map of the brick located in the corner of the ingot, where the seed was partly melted because of faulty control during the melting stage. It is obvious that the right part of the figure with the remaining seed has a longer bottom red zone compared with the left part of the figure without the remaining seed. The length of the red zone on the right increases with the thickness of the remaining seed. It is obvious that a high impurity concentration was obtained in the remaining seeds due to the diffusion in the melting process, resulting in a low carrier lifetime in this region. Thus, the height of the remaining seeds affects the length of the bottom red zone. In this aspect, both the models proposed by Gao et al. [11] and Yu et al. [12] can provide explanation for this result since both diffusion processes mentioned in the models occur around the top surface of the remaining seed crystals. Although