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Characteristics and value enhancement of cast silicon ingots

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ABSTRACT

Casting technologies of multi-crystalline (mc) silicon ingots in photovoltaic industry are reviewed in this paper and three main types of cast ingots are introduced. Cell efficiency distribution of the three types of ingots, i.e. common mc-silicon ingots, mono-like silicon ingots and super high efficiency mc (S-mc) silicon ingots, is examined, calculated and compared. It is found that the cell efficiency distribution of the three types of ingots is different because of their different defect characteristics. Common mc-silicon is used as the study baseline. Both mono-like and S-mc wafers have significantly better cell performance. Solar cells made from mono-like wafers have high efficiency close to mono-crystalline CZ wafers, however, the efficiency distribution is wide. Meanwhile, S-mc silicon wafers have much narrower cell efficiency distribution than mc-silicon wafers and mono-like silicon wafers in the experiments.

Main defects affecting cell performance are studied and the theories of how grain size affects cell performance are discussed in the paper too. Moreover, several casting technologies which can be used to achieve even higher quality cast ingots to further increase solar cell efficiency are proposed. These new casting technologies only increase the manufacturing cost on a small scale, however, they will greatly boost the wafers value in the solar market and accelerate the progress of Grid Parity.

1. Introduction

In 1954, the first mono-crystalline silicon solar cell was developed in Bell Laboratories achieving a conversion efficiency of about 6% [1]. A half century later, because of high crude oil prices, the solar energy industry is developing at explosive speed. Currently, among all the commercial solar cells, more than 90% are made on silicon wafers. Therefore silicon is the mainstream material for the fabrication of commercial solar cells at present and it will still be in the near future [2,3].

Traditionally, mono-crystalline wafers and multi-crystalline wafers are the two most common silicon substrates for the fabrication of PV cells. Recently, new technologies and products have been developed which include cast mono-like silicon, high efficiency mc-silicon, string ribbon silicon [4], amorphous Silicon (α-Si) film [5], and others. In this paper, three types of silicon ingots made by casting technology are introduced. They are common mc-silicon ingot, mono-like silicon ingot and super high efficiency mc (S-mc) silicon ingot. After these ingots are processed into wafers and solar cells, defect mapping is conducted on wafer level and cell efficiency is tested on cell level. We then compare the performance of these three types of products and provide the explanations of why they behave so differently. Lastly, several casting technology directions to manufacture even higher quality silicon ingots to further increase cell efficiency are forecasted.

Compared to Czochralski (CZ) and Floating Zone (FZ) technologies for mono-crystalline silicon manufacturing, directional solidification casting technology is widely used to manufacture mc-silicon ingots in solar industry for its low cost and high throughput. Based on silicon crystal nucleation, growth and directional solidification principles [6], raw poly-silicon material is first melted at about 1400 °C, then silicon melt is cooled and solidified slowly from bottom to top by controlling the cooling rate and temperature gradient. At the beginning of solidification, large amounts of small-grain nucleus are generated on the crucible or seed and these small grains grow upward to form larger columnar grains.

The ratio of the solute concentration of certain elements in the melt to that in the solidified silicon is given by a segregation ratio. It has been proven that the segregation ratio of most impurities, such as Fe, C, N in silicon, is less than 1. Therefore, these impurities tend to stay in the silicon melt instead of the solidified crystal. In other words, impurities in silicon melt are higher than that in solidified silicon during the ingot growth process. The more

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Table 1
Typical parameters for mainstream silicon casting furnace.

Furnace generation	Furnace generation	Typical charge (kg)	Silicon ingot dimension (mm)	Silicon blocks quantity
1st	G4	250	$690 \times 690 \times 240$	16 (4×4)
2nd	G5	450	$840 \times 840 \times 280$	25 (5×5)
3rd	G6	>650	$1000 \times 1000 \times 350$	36 (6×6)

impurities stay in silicon melt, the purer silicon ingot would be obtained.

Directional solidification casting furnaces are widely used in commercial mc-silicon manufacture, which have the feature of large capacity, low energy loss, short process cycle and good product quality. By now, there are 3 mainstream generations of casting furnaces, which are widely used for mc-silicon ingot manufacture. They are G4 (4×4), G5 (5×5) and G6 (6×6), containing 16, 25 and 36 silicon blocks (156 mm $\times$ 156 mm) in one silicon ingot respectively. Table 1 shows the typical parameters of G4, G5, and G6 casting furnaces. In fact, in silicon ingot manufacturing, nearly 1000 kg poly-silicon charge is used in a G6 casting furnace. GCL is doing its best to research and develop new technologies and tools to obtain high yield and high quality mc-silicon ingots. Now G7 (7×7) and G8 (8×8) casting furnaces are available with poly-silicon charges of more than 1000 kg for G7 furnace and about 1500 kg for G8 furnace.

2. Materials and experimental methods

To compare crystal characters and cell performance, three ingots with the same height were casted in our experiments, which were a common mc-silicon ingot, a mono-like silicon ingot and an S-mc silicon ingot. In the experiment, the common mc-silicon was casted with the standard process of the directional solidification. The mono-like silicon ingot was casted using seed-assisted directional solidification process, in which some ⟨100⟩-oriented CZ silicon seed crystal with about 2 cm thick were used. The S-mc silicon ingot was casted using a new grain control technology of GCL. In the new process, the geometry modification of the casting furnace and the optimization of its heat field are made on the directional solidification casting system for better control of grain uniformity and grain orientation.

Then wafers were sliced using a multi-wire slicing machine, with the thickness of 200 μm and dimensions of 156 mm $\times$ 156 mm from these three silicon ingots, separately. After that, all the wafers were made into solar cells.

In the experiments, the center blocks from the three ingots were used to examine the dislocation density. Wafers from the top, middle and bottom of the block were selected to investigate the dislocation density trends. After they were made into solar cells, cell efficiency was tested and compared.

Grain maps and features of different types of wafers were obtained using the commercially available Gemini Grain Size Analysis tool equipped with a matrix camera and 20 fast switching LED illuminations. To determine the grain distribution in a wafer, a 5 s acquisition time was used for each wafer.

Photoluminescence (PL) spectroscopy was used to observe the characterization of defects in silicon wafers and cells, which was proved to be a useful non-contacting and non-destructive technique in characterizing the distribution of defects and harmful impurities in semiconductor or solar wafer materials [7]. PL images of as-cut wafers have been acquired using the commercially available PL system equipped with a laser of 808 nm and a silicon CCD camera with a resolution of approximately 1 megapixel. 5 V laser voltage and a 20 s acquisition time were used during PL imaging. Dislocation density was automatically calculated from the PL images using the commercial software coming with the PL tool.

For solar cell manufacture, the following standard fabrication processes were included: (1) removal of damage layer on wafer surface, (2) texture, (3) phosphorus diffusion, (4) edge etching, (5) deposition of SiNx film on the front surface, (6) screen printing the rear Ag electrodes, rear Al paste, and front Ag electrodes, and (7) firing in a beltline furnace. It should be noted that in the texture process, alkali solution was used to form 'inverted pyramid' texture on mono-like silicon wafers' surface, and acid solutions were used to form 'worm-like' texture on the mc-silicon and S-mc silicon wafers' surface.

3. Characteristics of common mc-silicon wafers

In PV industry most multi-crystalline silicon ingots are produced using casting technologies. In Fig. 1(a), a PL image of a typical mc-silicon block is shown. We can find that there are many columnar crystals in the mc-silicon ingot. And the number of grains in a bottom wafer (Fig. 1(b)) is much more than that in a top wafer (Fig. 1(c)). Large amount of small grains with random orientations are formed on the crucible at the beginning of solidification. The controlled temperature gradient in the furnace favors certain orientations and the grains with those orientations grow large faster and overtake the grains growing slower. In fact, large amounts of silicon grains dissolve during the ingot growth process, only some special oriented grains survive in the end. So, we can find some larger grains in the top wafers, such as in Fig. 1(c).

A cast mc-silicon ingot has several special characters in its grain structure as the following:

1. It has large grains with size from several mm to several cm. For bottom to top, it has columnar crystal character.
2. It has high density of crystallographic defects, such as grain boundaries, dislocations and so on.
3. It has higher concentration of carbon (C) and metal impurities compared to CZ silicon ingots.
4. It has much less oxygen concentration than CZ silicon ingots.

Fig. 2 shows normalized cell efficiency distribution of a common mc-silicon ingot. Acid solutions are used to form a 'worm-like' texture wafer surface in the solar cell process. The cell efficiency difference between the best and the worst wafers is more than 1.6%, with about 8 bins and each bin represents 0.2%.

In Table 2, typical cell efficiency characters made of common mc-silicon, S-mc silicon, mono-like silicon and mono-silicon wafers were shown, which tells that common mc-silicon PV cells have much lower cell efficiency performance than mono-crystalline silicon PV cells. This is because common mc-silicon has significantly higher defect density and impurities concentration in its bulk materials than mono-crystalline silicon ingot. However, mono-like silicon PV cells have nearly the same cell efficiency as mono-crystalline silicon PV cells. We will discuss the features and characters in the next section.

PL images of common mc-silicon wafers are shown in Fig. 3, in which we found some dark lines and dark line clusters. The dark areas in PL image mean there are strong recombination centers of minority carriers [8] in the silicon material. The recombination centers, which are also called minority lifetime killers, are always induced by heavy metal impurities or defects in silicon bulk and have significantly negative impact on PV cells efficiency. We learned that dark clusters in bulk silicon (not edge or corner blocks) are typically caused by defects, such as dislocations [9]. Wafers in Fig. 3(a), (b) and (c) are selected from bottom, middle