

Influence of different vacuum conditions on the distribution of insoluble inclusions in a multi-crystalline silicon ingot



Shi Qiu ^a, Shiqiang Ren ^b, Liuqing Huang ^a, Tianyu Tang ^a, Ming Fang ^{a,b}, Xuetao Luo ^{a,*}

^a Fujian Provincial Key Laboratory of Advanced Materials, College of Materials, Xiamen University, Xiamen 361005, China

^b School of Material Science and Engineering, Dalian University of Technology, Dalian 116023, China

ARTICLE INFO

Article history:

Received 20 December 2015

Received in revised form

11 March 2016

Accepted 12 March 2016

Available online 14 March 2016

Keywords:

Directional solidification

Vacuum

Multi-crystalline silicon

Nitrides

Carbides

ABSTRACT

The distribution of insoluble inclusions in multi-crystalline (*m-c*) silicon was investigated by directional solidification under different vacuum conditions using recycled scraps. We found an abnormal peak (weight ratio of 1.19%) of SiC and Si₃N₄ with an average size of 100 μm located at the bottom of the silicon ingot obtained under low-vacuum conditions. At the top of the ingot, the impurity phase featured a weight ratio exceeding 10.62% and a size of 20 μm. Results showed that large particles sank to the bottom of the ingots whereas small particles floated upward. Further investigation suggested that the dominant factor influencing inclusion distribution is related to the presence of metallic impurities (e.g., Ca, Al, and Na) and their corresponding microstructure. A mechanism of migration was proposed to reveal that bonding of metallic impurities and insoluble inclusions contribute to the abnormal distribution of impurities. The results provide guidance for controlling the distribution of insoluble inclusions in recycled *m-c* silicon.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Multi-crystalline (*m-c*) silicon, one of the main materials used to manufacture solar cells, must show acceptable contamination levels in solar-grade silicon products [1–3]. Metallurgical methods are environment-friendly and inexpensive *m-c* production operations that aim to purify silicon from metallurgical-grade (99%) to solar-grade (99.9999%) [4]. Extensive efforts have been exerted to remove impurities, such as Al, Ca, Fe, B, and P, from metallurgical silicon effectively [5–7]. However, insoluble inclusions (including SiC and Si₃N₄) in silicon have yet to be sufficiently investigated to fulfill the requirements of the photovoltaic industry. During block casting, insoluble inclusions frequently appear in certain portions of silicon ingots [8,9]. The presence of SiC leads to severe ohmic shunt current flow in large-angle grain boundaries, causing degradation in solar cell efficiency [10,11]. Broken wires caused by insoluble inclusions result in wafer defects [12]. Both SiC and Si₃N₄ can induce impurity accumulation, which causes larger local defects in the final wafers [13,14]. Methods to recycle silicon scraps

with large amounts of insoluble inclusions have yet to be reported.

Insoluble inclusions are expected in ingots, which feature various contamination sources, including silicon scraps recycling, Si₃N₄ coating, dust particles on the long-term insulation plate, and reactions of the silica crucible and the graphite supporter [12,14–16]. Therefore, the behavior of insoluble inclusions in a silicon ingot must be understood to improve the solar cell efficiency of wafers. Researchers have investigated a number of insoluble inclusion characteristics, including their existing forms, sizing, distribution, and segregation behavior, near the solid–liquid interface during directional solidification [17–22]. However, previous studies have only concentrated on individual particles of insoluble inclusions during normal directional solidification (DS) (non-vacuum conditions). Other impurities, such as volatile impurities (e.g., Ca, Na) and non-volatile impurities (e.g., Fe, B), may also be found in *m-c* silicon. Removal of volatile impurities has been investigated by considering the segregation behavior and evaporation mechanism of DS under low-vacuum conditions [23–27]. Considering that the interactions of impurities with each other influence the corresponding redistribution, studying the behavior of insoluble inclusions while accounting for the existence of other impurities are a significant endeavor.

In this paper, the distributions of insoluble inclusions and other impurities along the height of an ingot were measured. Interactions

* Corresponding author. Fujian Key Laboratory of Advanced Materials, College of Materials, Xiamen University, No. 422, Siming South Road, Xiamen, Fujian 361005, China.

E-mail address: xuetao@xmu.edu.cn (X. Luo).

between insoluble inclusions and volatile impurities were studied during DS under low-vacuum and non-vacuum conditions in *m*-silicon.

2. Experiment

A pilot-scale electromagnetic induction furnace (DPS-650) was used to produce a silicon ingot, which is shown in Fig. 1. A graphite heater wound with copper coils absorbed the majority of the magnetic flux and generated heat by electromagnetic induction. A protective layer of Si_3N_4 was painted on the inner wall of a cylindrical silica crucible ($\Phi 810 \text{ mm} \times 620 \text{ mm}$) to act as a barrier for impurities and relieve thermal strain from silicon. An insulation plate on top of the silicon was designed to reduce carbon contamination from graphite components. Heater was used to control temperature field in the furnace chamber. During the DS process, silicon, as well as the crucible, moved downwards gradually from the hot zone to the cold zone. The increasing of crucible pulling down heights led to larger heat dissipating area at the bottom of silicon. Maintaining the net heat flux along axial direction was in favor of generating a vertical, homogeneous, columnar grain structure. Two thermocouples were adopted to monitor temperature fields in the furnace. Thermocouple 1 (TC1) was installed on the surface of the graphite heater to record the heater temperature, while thermocouple 2 (TC2) was installed at the bottom of the crucible to confirm melting completion.

The DS process involved three stages: melting stage, crystallization stage and cooling stage. In melting stage, the insulator was closed. Heater temperature increased gradually to 1850 K, and then maintained the temperature until melting completion. In crystallization stage, heater temperature decreased to 1800 K, and the crucible started pulling downwards. Heat was transferred to the bottom of crucible wall. Temperature gradient from bottom to top of silicon melt was formed. Crystal growth occurred once the temperature decreased to melting point of silicon. The height of crystal growth was measured by a quartz rod immersing into the molten silicon every hour. The solidified stage was considered

completed with the same measured value for three times, then entered into the cooling stage. Crucible didn't pulling downwards continually, and heater temperature decreased gradually to room temperature.

Silicon feedstock originated from the edges, head, and tail of the ingots, which included large amounts of foreign inclusions. Fig. 2 shows the process parameters of vacuum degree and solidified height during the DS process. In the melting stage, a protective atmosphere of argon was flowed and the pressure increased gradually to $6 \times 10^4 \text{ Pa}$. At the start of the crystallization, argon also flowed under a pressure of $6 \times 10^4 \text{ Pa}$ until the solidified height reached 50 mm. The furnace chamber was then evacuated to 0.3 Pa in 30 min, and the vacuum degree was maintained until the end of crystallization. In cooling stage, the pressure of argon increased to $6 \times 10^4 \text{ Pa}$ again. It should be noted that the crystal growth rate, or the ratio of solidified height to solidification time, was controlled to a constant value to ignore the influence of crystal growth rates on the segregation behavior of impurities.

After cooling down, the grown ingot (410 kg, $\Phi 810 \text{ mm} \times 350 \text{ mm}$) was cleaned by abrasive blasting and sectioned by a mechanical saw. Two axial rods close to the center region were selected for subsequent tests. For on silicon rod, nine pieces axial direction were chosen to be completely etched off with an acid mixture of HNO_3 and HF (1:1), followed by filtration and weighing. For further identification, a scanning electron microscope (SEM; Hitachi SU-70, Japan) with an energy dispersive spectrometer (EDS; INCAE250, Oxford, England) was employed to investigate impurity components of silicon rods and the acid-etched residues. The other silicon rod was equally divided into 34 blocks, and eight pieces ($10 \times 10 \times 10 \text{ mm}^3$) along the axial direction were selected to determine impurity concentrations by inductively couple plasma mass spectrometry (ICP-MS; DRC II, Perkin Elmer, US).

3. Results

The weights of initial samples with different solidified heights and corresponding insoluble inclusions after acid etching are shown in Table 1. Under the non-vacuum condition (solidified height of 0–30 mm), no residues are collected. Under the low-vacuum condition, three regions are found along the DS direction: insoluble precipitation at the start of solidification (50 and 60 mm), empty space (80–300 mm), and a large amount of

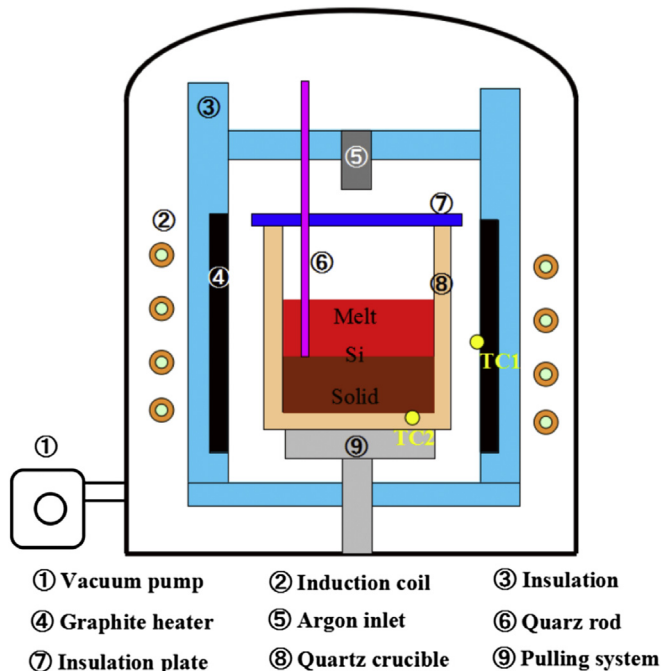


Fig. 1. Schematic of the pilot scale apparatus.

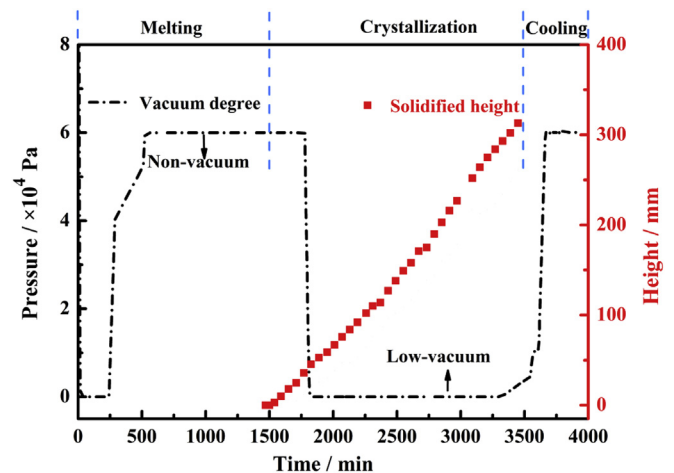


Fig. 2. Process parameters of vacuum degree and solidified height during the DS process.

Download English Version:

<https://daneshyari.com/en/article/1689131>

Download Persian Version:

<https://daneshyari.com/article/1689131>

[Daneshyari.com](https://daneshyari.com)