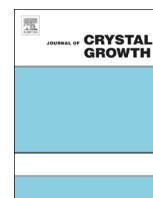




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## Journal of Crystal Growth

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# Natural sedimentation of insoluble particles during directional solidification of upgraded metallurgical-grade silicon

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## ARTICLE INFO

### Article history:

Received 21 November 2015

Received in revised form

31 December 2015

Accepted 3 January 2016

Communicated by P. Rudolph

Available online 12 January 2016

### Keywords:

A1. Directional solidification

B1. Insoluble particle

A1. Sedimentation

A1. Upgraded metallurgical-grade silicon

## ABSTRACT

Upgraded metallurgical-grade silicon is used to cast an ingot by directional solidification. Black shadows are randomly distributed in the ingot, and the shadows are caused by natural sedimentation of insoluble particles. The insoluble particles mainly consist of SiC and Si<sub>3</sub>N<sub>4</sub>. SiC and Si<sub>3</sub>N<sub>4</sub> exist as foreign particles and mainly sedimentate at the bottom of the ingot, not generating during directional solidification. Melt convection performs an important role in the sedimentation, resulting in the insoluble particles in the ingot center more than the nearby. Interestingly, since SiC and Si<sub>3</sub>N<sub>4</sub> will not be the recombination center of the minority carrier, the insoluble particles do not have a significant influence on the minority carrier lifetime. In particular, the sedimentation is discussed according to the thermodynamics and kinetics in detail.

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## 1. Introduction

Traditional energy sources, such as coal and fossil oil, are limited and polluted. Therefore, it is significantly important for humans to find new energy sources which are environment friendly and relatively high-efficiency. Solar energy is one of the promising sources among the currently known clean and renewable energy sources. Nowadays, more than 60% solar cells are made of multi-crystalline silicon [1]. In order to meet the application standards in solar cells, the purity of multi-crystalline silicon needs to reach at least 99.9999%. So far, there exist two main ways of purifying silicon, namely, a chemical method and metallurgical method (physical method) [2]. The chemical method is relatively costly and polluted, though it has been a mature technology. As for the metallurgical method, even though there are some problems which are difficult to overcome, however, it is relatively cost-effective and environment friendly. Therefore, it is worth of further studying and modifying the metallurgical method.

Directional solidification, one of the important metallurgical methods, is often used to cast or remove metallic impurities for multi-crystalline silicon ingot [3,4]. However, insoluble particles, which are hard to be removed, are often found in the multi-crystalline silicon ingot. The insoluble particles mainly consist of

SiC and/or Si<sub>3</sub>N<sub>4</sub>, which have an influence on mechanical properties and photoelectrical conversion efficiency [1,5]. The insoluble particles exist in the ingot by several routes as below: 1) they are generated by the segregation and accumulation of carbon and nitrogen for their equilibrium distribution coefficients are less than 1 [6,7]; 2) the particles result from coatings painted on quartz crucible [8]; 3) carbon dissolved from graphite resistance heaters chemically react with gaseous silicon compound under the high temperature [9]; 4) the particles stem from feedstock and exist as foreign materials [10].

Although there are so many reports on the insoluble particles, most of them focused on the segregation of carbon and nitrogen and microstructure of the insoluble particles [1,3–7]. The feedstock they used to study is purified by the chemical method. Compared with the metallurgical method (physical method), very few insoluble particles are generated for the chemical procedure is not in favor of producing SiC and Si<sub>3</sub>N<sub>4</sub> [11]. In consequence, the insoluble particles in their experiments are mainly generated by segregating and supersaturating of carbon and nitrogen during directional solidification, and the segregation behavior gives rise to the particles focused on ingot upper middle part. However, if feedstock is refined by the metallurgical method, SiC and Si<sub>3</sub>N<sub>4</sub> are easily generated for molten silicon is in contact with slag, graphite crucible or Si<sub>3</sub>N<sub>4</sub>-coated quartz crucible [8–10,11]. If the insoluble particle exists as a foreign material during the solidification, we think that its behavior is similar to the sedimentation of mineral in the earth crust for its density is heavier than that of molten silicon. While few of them were studied from this point of view. Trempa

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et al. observed SiC segregates during directional solidification and distributes at the middle and upper of silicon ingot in the experimental scale [12], but in our industrial experiment, we always observed the great majority of SiC and  $\text{Si}_3\text{N}_4$  sedimentate in the bottom of the ingot.

In the present paper, we investigate the cause of the insoluble particles, and discuss sedimentation according to the thermodynamics and kinetics. We also discuss the effect of convection on the sedimentation. Interestingly, the insoluble particles are found have no obvious influences on the minority carrier lifetime.

## 2. Experiments

The configuration of a multi-heaters directional solidification furnace (JS-540) is shown in Fig. 1. Quartz crucible is painted by  $\text{Si}_3\text{N}_4$  coatings to prevent impurities from the crucible, with the outer size of  $1000 \times 1000 \times 540 \text{ mm}^3$  and the wall thickness of 20 mm. The crucible is supported by graphite blocks. At the top of crucible, a carbon fiber plate is fixed to protect silicon from contaminating by the thermal decomposition of graphite resistance heaters. Argon gas is imported through a graphite tube into the furnace to protect the silicon from being oxidized at high temperature. Thermocouple 1 (TC1) is installed near the surface of top heaters to measure the furnace chamber temperature, and thermocouple 2 (TC2) is installed through the directional solidification block to measure the temperature at the crucible bottom. A quartz rod is inserted from the furnace top into the crucible to detect the crystal growth rate during solidification. The furnace chamber pressure is maintained at about 600 mbar ( $6 \times 10^4 \text{ Pa}$ ) by adjusting the import and export of argon flow. The furnace wall is cooled by water and it is considered as a constant temperature boundary. Thermal field is controlled by two ways: 1) controlling the power of graphite resistance heaters; 2) adjusting the insulation cage upward or downward.

Feedstock, 720 kg upgraded metallurgical grade silicon of about 5 N purity, was used to conduct in the present experiment. The feedstock was washed to remove contamination and then dried at 378 K about 12 h to remove water in large pieces or bricks. After that, the feedstock was loaded into the crucible and melted. During melting, the insulation cage was closed entirely. The furnace chamber was about 1823 K after 415 min. The temperature then decreased gradually to 1698 K. After this step, the furnace chamber temperature was controlled appropriately by a combination of

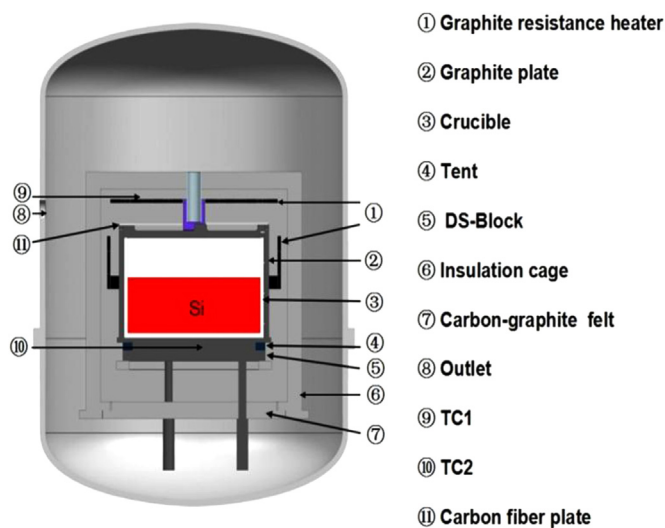


Fig. 1. Schematic configuration of the directional solidification furnace.

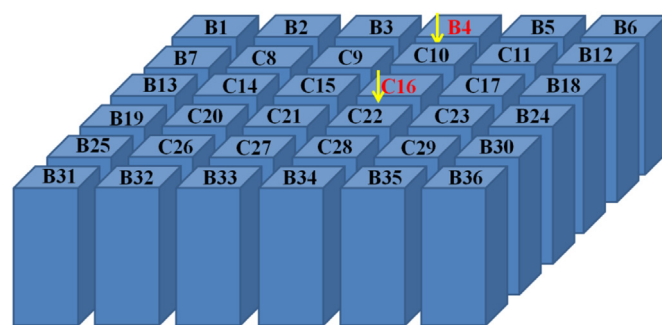


Fig. 2. Schematic of 36 bricks; in order to detect the presence of insoluble particles and the minority carrier lifetime, bricks B4 and C16 are taken out to be measured by infrared transmission imaging and  $\mu$ -PCD. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

resistance heaters and the insulation cage, and solidification was initiated. Finally, the temperatures at the top and bottom of the furnace chamber were about 1690 and 1267 K, respectively. Meanwhile, solidification ended. After annealing, the furnace was directly cooled to ambient temperature.

After demolding, the ingot was cut into 36 bricks with the dimensions of  $156 \times 156 \times 13.5 \text{ mm}^3$  as shown in Fig. 2. The average resistivity of the bricks is  $0.52 \Omega \text{ cm}$ , with P-type conduction. In order to detect the presence of insoluble particles, bricks C16 and B4, which typically represent the central section and its nearby section of the ingot, were examined by infrared transmission imaging (SEMILAB, IRB 50). The minority carrier lifetime of the two bricks were measured by microwave photo-conductivity decay technique ( $\mu$ -PCD, SEMILAB WT 2000). The detection face were marked with yellow arrows as shown in Fig. 2.

## 3. Results and discussions

### 3.1. Natural sedimentation of insoluble particles

#### 3.1.1. Cause of the insoluble particles

The representative infrared transmission images of the bricks B4 and C16 are shown in Fig. 3(a). The bottom area of the bricks is fully covered with dark shadows, which are labeled by a red thick line. Besides the shadows at the bottom, a bandage-shaped dark shadow at approximately 80% height is observed, marked with a red light line. In particular, above the red thick line, an irregular dark shadow in brick C16 is observed, which is tagged by a red ellipse. In a word, the shadows are distributed randomly. Fig. 3(b) is the corresponding infrared transmission images. Since silicon crystal is transparent to infrared light, the dark shadow regions show where the inclusions exist.

The dark shadows were further examined. A sample (corresponding to the dark shadow regions), cross-sectional cut at the height of 20 mm, was taken out from brick C16 to be examined by SEM (Scanning Electron Microscope, SU-70, Hitachi, Japan) equipped with EDS (energy dispersive X-ray spectroscopy, INCAE250, Oxford, England). Fig. 3(c) and (d) shows typical microstructure of the sample. We can clearly observe that irregular or amorphous particles embed the main body with the size of micrometers, and a smooth porosity around the particle as shown in Fig. 3(c). SiC and  $\text{Si}_3\text{N}_4$  are known as insoluble particles in the melt during the directional solidification of multi-crystalline silicon.

According to the C–Si phase diagram and small equilibrium distribution coefficient of carbon, Hsieh et al. [1]. consider that carbon accumulates at solid–liquid interface when crystal grows, and carbon reacts directly with silicon to generate SiC when it

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