Applied Thermal Engineering 106 (2016) 875–880

Contents lists available at ScienceDirect

Applied Thermal Engineering

journal homepage: www.elsevier.com/locate/apthermeng

Research Paper

Removal of metal impurities by controlling columnar grain growth during directional solidification process

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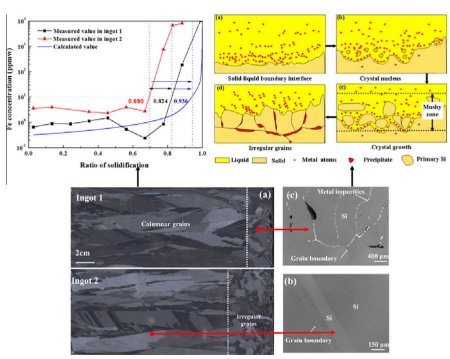
HIGHLIGHTS

- Growth of columnar grains is effectively controlled by temperature gradient.
- Columnar grains can improve the ratio of the high-purity area.
- Metal impurities form a mushy zone in front of the solid-liquid interface.
- Formation mechanism of impurities precipitation in irregular grains is discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 March 2016
Revised 4 June 2016
Accepted 6 June 2016
Available online 7 June 2016

Keywords:
Crystal morphology
Columnar grains
Metal impurity
Directional solidification

ABSTRACT

Silicon ingots with columnar grains and irregular grains as raw material for solar cells were obtained by directional solidification. The relationship between crystal morphology and concentration of metal impurities was studied. The result shows that columnar grains can improve the ratio of the high-purity area, where the concentration of metal impurities is less than 10 ppmw and more consistent with the calculated value by the Scheil's equation. Meanwhile, the metal silicide precipitates at the irregular grain boundaries. Large temperature gradient at the solid-liquid interface dedicated to the stability of solid-liquid interface, which is conductive to the growth of the columnar grains. High concentration of metal impurities introduces a large constitutional supercooling to reduce the stability of solid-liquid interface, then further form a mushy zone in front of the solid-liquid interface, which leads to the growth of irregular grains.

1. Introduction

So far, the photovoltaic industry which is rapidly developed demands a large number of solar grade silicon (SoG-Si) as raw material for solar cells [1,2]. There are metal impurities in the solar cells, which deteriorates the electrical properties of silicon material, such as electrical resistivity [3] and minority carrier lifetime [4–6]. Metallurgical route becomes a popular method for the preparation of SoG-Si because of its low coast [7] and environmentally friendly [8]. Directional solidification is one of popular method in the metallurgical route, which removes metal impurities with a low segregation coefficient [9]. During directional solidification process, metal impurities segregate at

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http://dx.doi.org/10.1016/j.applthermaleng.2016.06.037
1359-4311/

the solid-liquid interface and concentrate on the liquid phase due to their lower solubility in solid than in liquid. The concentration of metal impurities in earliest solidification area is far less than initial concentration. Because most metal impurities are removed to the top of silicon ingot by directional solidification.

The concentration of metal impurities in the earliest solidification area can be affected by many factors such as magnetic fields [10,11], vacuum condition [12], the rate of crystal growth [13] and so on [14,15]. Autruffe et al. [16,17] have indicated that impurities segregate towards grain boundary. The silicide of metal impurities depends on grain boundary character and microstructure in Mc-Si [18]. Ma et al. [19,20] have revealed that the solid-liquid interface shape plays an important role on the control of crystal quality during the crystal growth process. There is a larger grain size, vertical columnar structure, fewer defects in the silicon ingot with a suitable growth of the solid-liquid interface. Tan et al. [21] have revealed that columnar grains are affected by the constitutional supercooling in the solid-liquid interface. Most work above has been studied to control the crystal morphology in the silicon ingot by directional solidification. However, the relationship between the crystal morphology and the concentration of metal impurities has not been revealed during directional solidification.

In this paper, two silicon ingot with columnar grains and irregular grains are obtained by directional solidification, respectively. The concentration distribution of metal impurities in the different crystal morphologies is measured to study the relationship of the concentration of metal impurities and the crystal morphology. The effect of columnar grains on the removal of metal impurities in MG-Si during directional solidification process is also revealed.

2. Experimental

Experiment was conducted in an industrial directional solidification furnace. Fig. 1 shows the schematic diagram of the experimental apparatus. It consists of vacuum system, melting system, insulation system, heating exchange system. During the directional solidification process, the temperature of heater slowly decreases while the insulation system moves upwards and the quartz crucible remains stationary on the heat exchange block. Then the heat in molten silicon flows only along axial direction and is taken away by the heat exchange block, so that the silicon crystal grows from the bottom to the top. In this experiment,

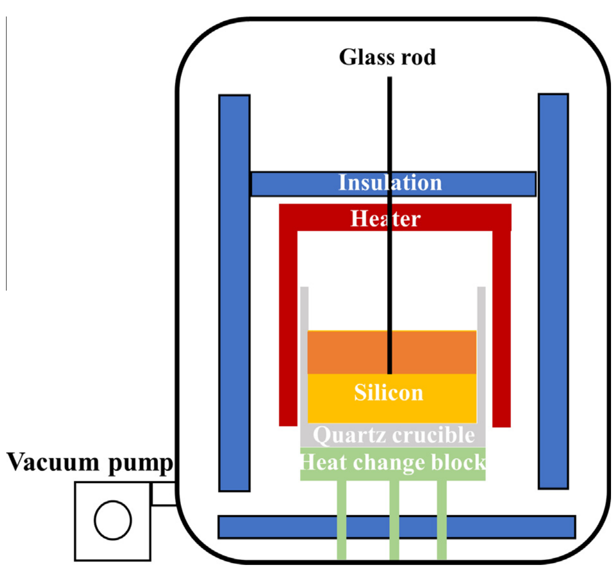

Fig. 1. Schematic diagram of the experimental apparatus.

two silicon ingots were obtained by different production process which includes different temperature of heater and the changing structure of heat change block.

MG-Si as the raw material was used in this experiment. The concentration of metal impurities in the raw material is about 1000 ppmw. The concentration of Fe is the main impurity in the raw material, as shown in Table 1. Prior to processing by directional solidification, more than 600 kg MG-Si was washed sufficiently with water to remove possible solid residues and extraneous impurities from the surface. Subsequently, it was placed in a quartz crucible with an inner dimensions of $800 \times 800 \times 480$ mm, and then the chamber was full of flowing argon with a certain pressure 6×10^4 Pa. Then the insulation was pulled upwards when the rate of crystal growth was from 6×10^{-7} m/s to 4×10^{-6} m/s until the molten silicon solidified completely. The rate of crystal growth was measured by the glass rod.

The two silicon ingot obtained by above process are about dimension of $800 \times 800 \times 190$ mm. Two silicon blocks were cut parallel along the growth direction from the center regions of the two silicon ingots for observation, as shown in Fig. 2. Silicon block is cut from the center region of the ingots which is outlined in black line. The samples were cut from the bottom to the top of the silicon block by diamond saw. The impurity concentrations of each sample were determined by Inductively Coupled Plasma Mass Spectrometer (ICP-MS), Scanning Electronic Microscopy (SEM) and Electron-probe Micro-analyzer (EPMA).

3. Result and discussion

3.1. Crystal morphology

The macro crystal morphology of the two silicon blocks which parallel along the growth direction is shown in Fig. 3(a). There are columnar grains and irregular grains in the two silicon ingots. Ingot 1 and 2 have columnar grains, which are from bottom to top of the silicon ingot. The height of columnar grains in ingot 1 is 170 mm, while that in ingot 2 is 150 mm.

The micro-crystal morphologies in the columnar and irregular grains are different and shown in Fig. 3(b) and (c). There are not precipitates of metal impurities in the columnar grains, as shown in Fig. 3(c). The diameter of columnar grains is obviously different. The smallest diameter is about 400 μm, while the largest diameter is up to 2 cm. The precipitate of metal impurities is found in the top of silicon ingot. The morphology of metal impurities in the top of silicon ingot is shown in Fig. 3(b), which means that the concentration of metal impurities in the top of ingot is so high that they precipitate. The metal impurities are more inclined to precipitate in the grain boundaries and they are discrete in 2-D coordinates. There is only irregular grains in the top of the silicon ingot. Compared with the size of the columnar grains, the size of irregular grains is smaller. It is worked out that the metal impurities should influence the crystal morphology during the directional solidification process.

The microstructure of the precipitate phase is shown in Fig. 4. There are obviously boundaries in the precipitate phase. It means that the precipitate phase consists of three kinds of metal elements, Fe, V and Ni, as shown in Fig. 4(b)–(d). They precipitate in the same location. The concentration of metal impurities in the depositing area are shown in Table 2. In the Fe depositing area, the precipitation phase is $FeSi_3$, because the concentration of Si is three times of that of Fe. In the V depositing area, the main metal impurities are Si and V. Furthermore, there is a certain concentration of Ti in the area. The precipitation are VSi_2 and $TiSi_2$, respectively. Because the concentration of Si is about twice of the total concentration of V