The impact of the solidification rate on purification polysilicon by directional solidification

Tao Lin¹, Chun Yan Duan¹,²

¹Department of Electronics and Information, Foshan Polytechnic, Foshan 528137, P. R. China
²lintao@fspt.edu.cn, dcylgang@163.com

Abstract: In this experiment, directional solidification method was used to prepare metallurgical grade silicon ingot. We have studied the solidification rate which influenced the results of the experiment. Experimental results showed that the impurities were concentrated mostly in the top of silicon ingot. It was inferred that second or more times directional solidification experiments is needed to remove the impurities. What’s more, it showed that the best solidification rate is 1.5mm/min in this study.

1. Introduction

As we all know, solar grade silicon is the main material for photovoltaics. The purification of solar-grade silicon is a hot spot in current social research. At present, more than 85% of polysilicon in the world is produced by the modified Siemens method, but modified Siemens method is very expensive and energy consumption is high, so researchers has apply themselves to develop new methods to prepare poly-crystal silicon. Metallurgical method has the advantages of low energy consumption and cheapness, so it becomes a hot spot in research nowadays.

The global energy consumption is predicted to grow dramatically year by year[1]. The world's energy shortage limits economic development. So new energy has been widely studied in recent years, such as the photovoltaic industry. Solar energy is one of the most important renewable energy sources in the world. The biggest feature of solar energy is its huge energy. On the earth, there is no energy comparable to solar energy[2]. Solar grade silicon is the material foundation for the photovoltaic industry, The purification of solar-grade silicon is a key point in current research. Metallurgy is the most important method among these methods, Metallurgical method has high output rate and low investment threshold.

The process of purifying solar-grade silicon by metallurgical method mainly includes slag refining, pickling, solidification refining, vacuum refining, plasma refining and alloy smelting purification. Usually, the metallurgical method uses industrial silicon as a raw material.

Alloy slagging is similar to directional solidification in the principle, It virtually structure the balance between Si-M(M on behalf of other metal) liquid phase and Si, then the segregation coefficient of the solid phase and liquid phase will be changed, So the impurities can be removed.

Directional solidification is one method of metallurgy process. It is a technique to purify silicon by making the growth of ingot in a one-way and enriching the impurity elements to the top of the ingot under segregation effect by controlling the changes of temperature field. This method has very obvious effect on extraction of metallic impurities.

Directional solidification technology allows the solidified structure of the material to be arranged in
a specific direction, that is, the directional or single crystal structure, which can scientifically improve the mechanical and physical properties of the material. Due to the small segregation coefficient between solid and liquid silicon, it is an important process for removing metal impurities such as iron and titanium from silicon[3]. By controlling the temperature gradient, the silicon ingot grows unidirectionally, and the impurities are concentrated on the top of the ingot through the segregation effect.

In this article, we will remain cooling water flow rate at 500L/h, then we just changed the solidification rate. We will investigate it how to affect the impurity removing efficiency.

2.Experimental
In this experiment, #3303 MG-Si was used as raw material and the main impurities contents were shown in Table. 1.

| Element | B  | Al | P  | Ca | Ti | Cr | Mn | Fe  | Ni  |
|---------|----|----|----|----|----|----|----|-----|-----|
| content(mass/×10^{-6}) | 14.2 | 1640 | 61 | 290 | 711 | 12 | 271 | 2040 | 253.8 |

About 1kg #3303 metallurgical silicon blocks was placed into the quartz crucible and lay it into the intermediate frequency induction vacuum directional solidification furnace (DJGS-100). Then, the system was vacuumized to 10^{-3} Pa and then heat up the furnace by intermediate frequency induction to a certain temperature and keep the temperature for appropriate time. Infrared thermometer (DT-8869H) was used to observe the temperature of the reaction[4]. Afterwards, the cooling pole was switched on and the directional solidification was carried out. In this study, the cooling water flow rate and the solidification rate were shown in Table. 2.

| Experiment | 1   | 2   | 3   |
|------------|-----|-----|-----|
| the cooling water flow speed(500L/h) | 500 | 500 | 500 |
| the solidification rate (mm/min)    | 2.0 | 1.8 | 1.5 |

3.Characterization
The metallography and microstructure of the silicon were polished etch with sodium hydroxide for 20 minutes and determined by Polarizing microscope (NIKON INSEC HCS601).

4.Results and Discussion
The digital photos of the silicon ingot were shown in Figure. 1(a)、1(b) and 1(c) .
Figure 1. The digital photos of silicon ingot after directional solidification. 
(a) the raw metallurgical silicon (#3303), (b) the solidification rate at 2.0 mm/min, (c) the solidification rate at 1.8 mm/min, (d) the solidification rate at 1.5 mm/min.

Compared to Figure 1(a), from the photo of Figure 1(b), we can see some quartz from the crucible was adhered to the outside surface of silicon ingot. From the photo of Figure 1(c), we can see a sheeny surface with a lot of ramiform crystals on it. From the photo of Figure 1(d), we would find that the surface of the silicon ingot was brighter than that of Figure 1(a), 1(b), and 1(c), the most obvious effect of solidification was the solidification rate at 1.5 mm/min.

Figure 2 gives the metallographic of the silicon crystal grown through the directional solidification rate at 2.0 mm/min, 1.8 mm/min, and 1.5 mm/min. From Figure 2(a) to Figure 2(c), the surface of the silicon crystal changed smooth steadily. In Figure 3(c), the surface of the silicon crystal is smooth and there are no obvious straight boundaries in the silicon grains. While there are some silicon grains have straight boundaries in Figure 2(b), which located in the center of the silicon ingot, across which the etching characteristics are different from each other. Some of the straight boundaries seem to be twins or stacking faults in 2(a). Figure 2(a), 2(b), and 2(c), the most obvious effect of solidification was the solidification rate at 1.5 mm/min.
5. Conclusions

(1) It showed that the impurities were concentrated mostly in the top of silicon ingot.

(2) It inferred that second or more times directional solidification experiments is needed to remove the impurities.

(3) It showed that the most obvious effect of solidification was the solidification rate at 1.5mm/min.

(4) It inferred that the less solidification rate it was, the best effect of solidification it became.

Acknowledgments

This work was financially supported by Foshan Intelligent Photovoltaic Product Engineering Technology Research Center.

References

[1] Zhou Huan, Yang Shaofeng, Wei Donglei, Liang Chunyong, Yang Qiang, Yang Huilin, Wang Donghui, Li Mingjun, Yang Lei. Development of hydrofluoric acid-cleared silicon nitride implants for periprosthetic infection eradication and bone regeneration enhancement. Materials science & engineering. C, Materials for biological applications, 2021, 127 {5}:

[2] Mineralogy; Reports from Kunming University Advance Knowledge in Mineralogy (Research on the Interaction of Ca, Al and Fe in Recovering and Purifying Silicon) [J]. Mining & Minerals, 2020, {4} {5}:

[3] Fan Yang, Jijun Wu, Wenhui Ma. Research on the Interaction of Ca, Al and Fe in Recovering and Purifying Silicon [J]. JOM, 2020, {4} (prepublish):

[4] Silicor Materials Inc.; Patent Issued for Method Of Purifying Aluminum And Use Of Purified Aluminum To Purify Silicon (USPTO 10,773,963) [J]. News of Science, 2020, {4} {5}: