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Removal of Carbon from Silicon Melt for Solar Cells
シリコンの脱炭に関する研究

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1. Introduction

One of the most prominent process for production of solar grade silicon is reduction of high purity silica by high purity carbon. Since carbon content of silicon obtained by this process is more then several hundreds ppmw, the quality of the product is not enough for the following processes of solar cell production, such as uni-directional solidification. Therefore, an inexpensive technique to remove carbon in silicon melt must be developed.

Several investigators have tried to remove carbon in liquid silicon, however positive results have not been reported[1]. This is because silicon forms oxides on the surface of melts even under low oxygen partial pressure and poisons the oxidation of carbon. Because carbon in silicon seems to exist mostly as fine SiC particles[2], the dissolution of carbon might determine the total rate of the reaction.

In this study, filtration of silicon melt and oxidation of carbon were investigated. We discussed thermodynamics of decarburization of silicon, which had not been considered properly.

2. Experimental

Samples of 0.1-0.2 wt% carbon were prepared by melting high purity polycrystalline silicon in a graphite crucible. Metallurgical grade silicon containing about 100ppmw carbon was used for experiments with silicon of lower carbon contents as well.

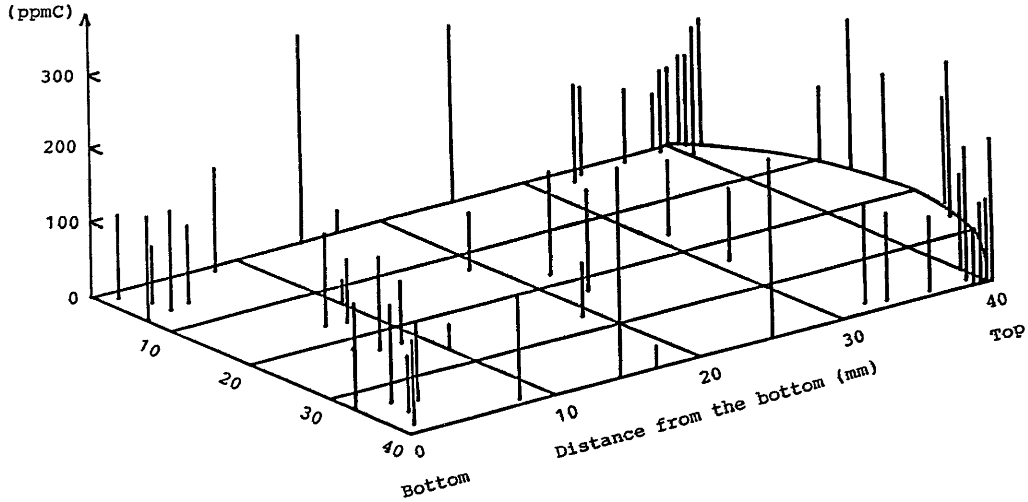

Fig. 1 Carbon distribution in quenched silicon melt.

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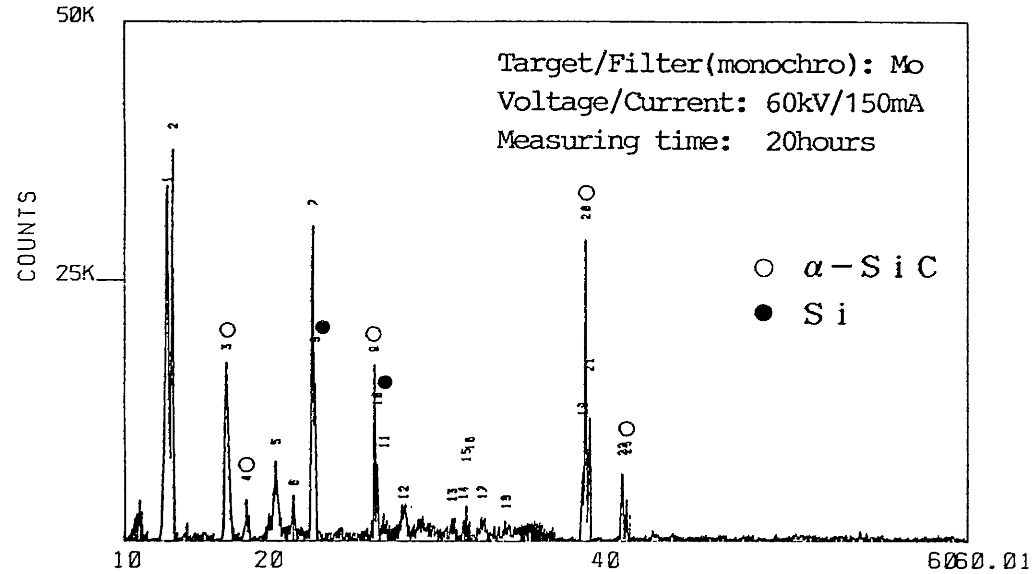

Fig. 2　X-ray diffraction pattern for the substance adhered to crucible wall.

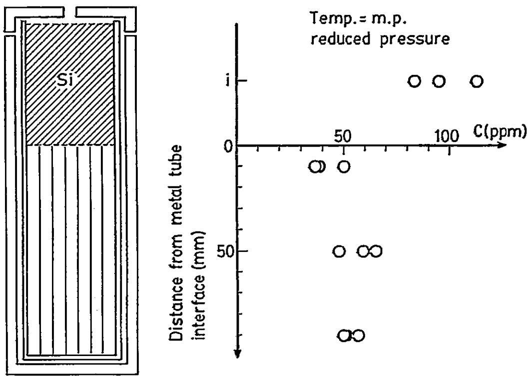

Fig. 3　Carbon distribution in filtering tubes.

The samples were placed in a silica crucible and heated directly by the high frequency induction to prevent possible contamination from heaters such as graphite.

The furnace was kept under the pressure of 0.7-1 torr by using vacuum pump. Samples were taken by sucking a silica tube. Temperature was measured by a two-colored pyrometer. The optical system including the window and the prism had been calibrated with black body furnace. Carbon analysis was carried out by combustion-absorptiometric method. High purity oxygen, free of hydrocarbon, was used as oxidizing gas to minimize the blank value[3].

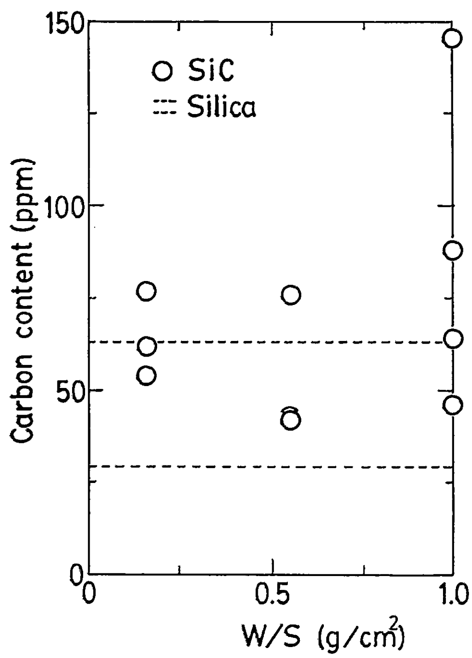

Fig. 4　Carbon content in filtered silicon as a function of the surface area of pellets per unit weight of silicon.

3. Carbon in silicon melt

Figure 1 shows the distribution of carbon in quen-

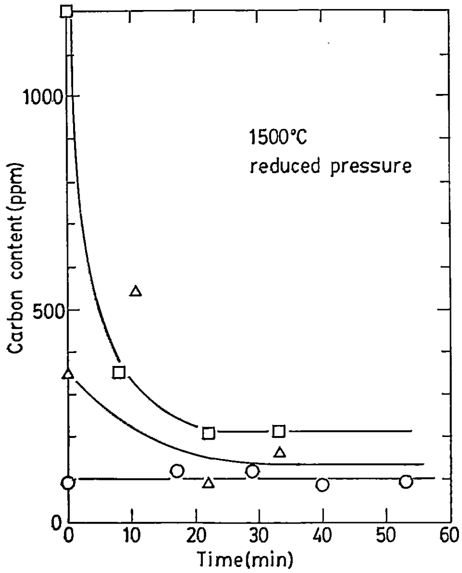

Fig. 5 Carbon content in silicon melt as a function of time.

ched silicon after melting in silica crucible for 10 minutes under reduced pressure at 1500°C. Initial carbon content was about 100ppmw. In some part of the melt, the carbon content was lower than the initial value whereas there were regions of higher carbon content. The distribution of carbon suggests that some reactions occurred at the surface of the melt, and there was a good chance that SiC particles might be segregated.

X-ray diffraction analysis confirmed the existence of SiC in the adhered substance at the crucible wall (Fig. 2). This indicates the possibility to remove carbon in silicon melt by mechanical trapping of SiC particles.

4. Mechanical removal of SiC particles

We used silica and silicon carbide as filtering materials. Figure 3 shows one of experimental results for silica tubes as filters. Carbon was reduced to about 50ppmw from the initial content of 100ppmw. Results for experiments using SiC pellets as a filter are given in Fig. 4.

Results by silica filters are shown by broken line in the same figure. Carbon was decreased to about 60ppmw, however, rather large scatters were observed. There were no such scatters for silica tube filter.

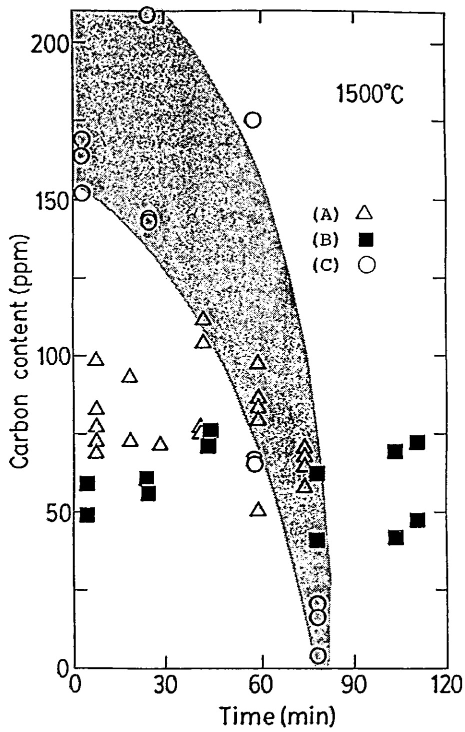

Fig. 6 Carbon content in silicon melt as af unction of time.

5. Removal of carbon by oxidation

5.1 Experimental aspects for decarburization by oxidation

Coexisting with silica yields the maximum oxygen partial pressure for Si-O system. Holding liquid silicon in silica crucible may be the simplest way. Since the highest oxygen partial pressure should be obtained at the surface, the melt should also be covered by silica. Removal of CO gas from the surface of silicon either by pumping of blowing inert gas may enhance the reaction rate.

5.2 Results

Figure 5 shows the results for the simple melting in silica crucible under reduced pressure. For the initial carbon content of 350 and 1200ppmw, it decreased to about 200 ppmw while from 100ppmw no apparent change was observed.

Figure 6 presents effects of addition of silica powder to the melt surface. Experiments were carried out as follows; (A) addition of silica powder to the melt surface: (B) Silica addition and smaller crucible

(ϕ42 * 66 mm h instead of ϕ42 * 150 mm h) to help the discharge of evolved CO gas: (C) silica addition, smaller crucible, Ar injection on the surface of the melt and the system is under the reduced pressure. As low as 10ppmw of carbon was obtained in the experiment (C).

6 . Conclusion

We have shown two types of technique to reduce carbon content in silicon melt. From metallurgical grade silicon of 100 ppmw carbon, we could obtain silicon with carbon content of about 50 ppmw by filtering silicon melt, and several ppmw by oxidation. Silica addition to the melt surface kept higher oxygen partial pressure and CO gas removal by inert gas prevents carbon reversion. These two points are the most important part of decarburization process.

Acknowledgement

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